

# TITLE OF THE INVENTION

SILVER HALIDE COLOR PHOTOGRAPHIC LIGHTSENSITIVE  
MATERIAL

## CROSS-REFERENCE TO RELATED APPLICATIONS

5           This application is based upon and claims the  
benefit of priority from the prior Japanese Patent  
Applications No. 2002-311604, filed October 25, 2002;  
No. 2003-60367, filed March 6, 2003; and  
No. 2003-326547, filed September 18, 2003, the entire  
10 contents of all of which are incorporated herein by  
reference.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

15           The present invention relates to a silver halide  
color photographic lightsensitive material. More  
particularly, the present invention relates to a silver  
halide color photographic lightsensitive material which  
is highly sensitive, is excellent in graininess and  
exhibits high sharpness.

### 20           2. Description of the Related Art

          With respect to the silver halide color  
photographic lightsensitive material, further  
sensitivity enhancement is being urged for increasing  
the user benefit of color negative films. Especially  
25 in recent years, the regular use of highly sensitive  
films of 800 or higher specific photographic speed (ISO  
speed) is being promoted in accordance with the

penetration of compact cameras with zooming capability and lens-equipped films which enable readily and easily coping with various exposure conditions.

5 This film sensitivity enhancement realizes an expansion of the photographing range of lightsensitive materials to, for example, photographing without the use of stroboscopic flash in dark rooms, fast-shutter photographing with the use of telephoto lens like sports photography, photographing requiring long-time  
10 exposure like astronomical photography, etc. Thus, the users can have tremendous benefits therefrom. Therefore, the sensitivity enhancement of films is one of everlasting themes to be tackled in this industry.

The conventional high-speed films have been those  
15 whereby only images of low grade far above the threshold of user's tolerance can be obtained as a result of the pursuit of sensitivity enhancement. Therefore, the users have been forced to choose between speed and image quality, and often the user's choice  
20 has resulted in having to take image quality rather than speed.

For enhancing the sensitivity of lightsensitive materials, it is old trick in this industry to increase the size of silver halide grains as photosensitive  
25 elements and further simultaneously employ other sensitivity enhancement technologies.

The sensitivity enhancement can be realized to a

certain level by an increase of the size of silver halide grains. However, as long as the content of silver halides stays constant, the size increase would inevitably lead to a decrease of the number of silver halide grains, namely, a decrease of the number of development initiation centers and would consequently cause a disadvantage of extreme graininess deterioration.

Moreover, a design intended to increase the number of silver halide grains per area, namely, an increase of the amount of silver halides used in light-sensitive material coating would invite such a problem that deteriorations of photographic performance, such as fog increase, sensitivity lowering and graininess deterioration, occur during the storage of light-sensitive material after production and before use thereof.

Meanwhile, recently, there has been disclosed a technology of achieving a sensitivity enhancement without detriment to graininess by incorporating a compound, the compound having at least three heteroatoms that do not react with oxidizing developing agents, in a silver halide photographic light-sensitive material (see, for example, Jpn. Pat. Appln. KOKAI Publication No. (hereinafter referred to as JP-A-) 2000-194085).

Tabular silver halide grains have been employed

for the sensitivity enhancement of light sensitive materials. With respect to the tabular silver halide grains, not only have processes for producing the same and technologies for use thereof been disclosed but  
5 also the advantages, such as improvements of the relationship of speed/graininess including an improvement of color sensitization efficiency by spectral sensitizing dyes, are known (see, for example, U.S.P. 4,434,226).

10 Extensive studies have been conducted for the performance enhancement of these advantageous tabular grains. Tabular grains of large equivalent circle diameter and reduced thickness are advantageous for the sensitivity enhancement from the viewpoint that  
15 spectral sensitizing dyes can be adsorbed thereto in greater amounts. The thinner the tabular grains, the greater the amount of adsorbed dyes. However, practically, attaining a sensitivity enhancement effect conforming to an increase of the amount of adsorbed  
20 sensitizing dyes becomes difficult in accordance with the reduction of grain thickness. As a reason therefor, there can be mentioned, for example, the influence of unfavorable electron trap within grains. Technologies for attaining sensitivity enhancement by  
25 removing the electron trap are disclosed (see, for example, JP-A-2001-281778).

However, even when these technologies are



employed, there occurs such a problem that the introduction of dislocation lines that are effective in sensitivity enhancement becomes difficult in accordance with the reduction of the thickness of tabular grains.

5 Thus, the intended sensitivity enhancement has not been attained. Therefore, there is a demand for a further technology attaining sensitivity enhancement.

On the other hand, it is known that the sharpness of lightsensitive materials can be improved by reducing the thickness of the protective layer thereof.

10 Further, it is described that the sharpness of lightsensitive materials can be improved by reducing the thickness thereof with the use of tabular grains (see, for example, JP-A-5-034857). However, the light

15 scattering by tabular grains per se is increased in accordance with the reduction of the thickness of tabular grains. Consequently, there has occurred such a problem that the reduction of the thickness of tabular grains employed rather leads to a deterioration

20 of the sharpness of lightsensitive materials.

Under these circumstances, it has been difficult to obtain a lightsensitive material that is highly sensitive by virtue of the advantage of tabular grains and simultaneously exhibits high sharpness.

#### 25 BRIEF SUMMARY OF THE INVENTION

The present invention has been developed with a view toward solving the above problems of the prior

art. It is an object of the present invention to provide a silver halide color photographic light-sensitive material that is highly sensitive, being excellent in graininess and exhibits high sharpness.

5           The object of the present invention has been attained by the following means.

          (1) A silver halide color photographic  
lightsensitive material comprising a support and,  
superimposed thereon, at least one blue-sensitive  
10   silver halide emulsion layer, green-sensitive silver  
halide emulsion layer, red-sensitive silver halide  
emulsion layer and protective layer, which silver  
halide color photographic lightsensitive material  
contains at least one compound capable of increasing  
15   photographic speed, the compound having at least three  
heteroatoms in its molecule, and wherein at least one  
layer of the silver halide emulsion layers comprises an  
emulsion, the emulsion consisting of a lightsensitive  
silver halide emulsion wherein 50% or more in number of  
20   all the silver halide grains are occupied by tabular  
grains having (111) faces as main planes, the tabular  
grains:

          (i) composed of silver iodobromide or silver  
chloriodobromide;

25           (ii) having an equivalent circle diameter of  
1.0  $\mu\text{m}$  or more and a thickness of 0.15  $\mu\text{m}$  or less; and

          (iii) composed of core portions of 0.1  $\mu\text{m}$  or less

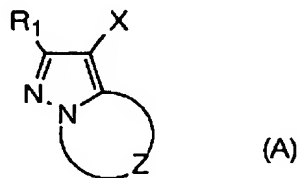
thickness free of growth ring structure and composed of silver iodobromide and shell portions having ten or more dislocation lines.

(2) The silver halide color photographic  
5 lightsensitive material according to item (1) above, wherein the sum of protective layer thicknesses is 3  $\mu\text{m}$  or less.

(3) The silver halide color photographic  
lightsensitive material according to item (1) or (2)  
10 above, wherein the compound capable of increasing photographic speed, the compound having at least three heteroatoms in its molecule, is a 1,3,4,6-tetraazaindene compound.

(4) The silver halide color photographic  
15 lightsensitive material according to any of items (1) to (3) above, wherein the compound capable of increasing photographic speed, the compound having at least three heteroatoms in its molecule, is represented by the following general formula (A) or general  
20 formula (B).

General formula (A)

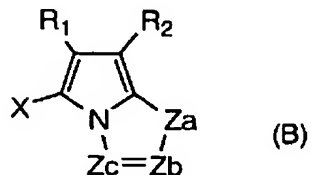


In the general formula (A),  $R_1$  represents a  
25 hydrogen atom or a substituent.  $Z$  represents a nonmetallic atom group required for forming a

5-membered azole ring containing 2 to 4 nitrogen atoms. The azole ring may have a substituent (including a condensed ring). X represents a hydrogen atom or a substituent.

5

General formula (B)



In the general formula (B), Za represents -NH- or -CH(R<sub>3</sub>)-. Each of Zb and Zc independently represents -C(R<sub>4</sub>)= or -N=. Each of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently represents an electron withdrawing group whose Hammett substituent constant  $\sigma_p$  value is in the range of 0.2 to 1.0. R<sub>4</sub> represents a hydrogen atom or a substituent, provided that when there are two R<sub>4</sub>s in the formula, the two R<sub>4</sub>s may be identical with or different from each other. X represents a hydrogen atom or a substituent.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in detail below.

First, the compound capable of increasing photographic speed, the compound having at least three heteroatoms in its molecule, according to the present invention (hereinafter also referred to as "compound of the present invention") will be described. Herein, the heteroatom comprehends any of the atoms other than

carbon and hydrogen, but is preferably selected from among nitrogen, sulfur, phosphorus and oxygen.

When the compound of the present invention is a heterocycle, the heterocycle means that three or more heteroatoms are present in constituent parts of a ring system, or means that at least one heteroatom is present in constituent parts of a ring system while at least two heteroatoms are present outside the ring system, namely, at positions separated from the ring system through at least one nonconjugated single bond, or part of further substituents of the ring system.

In the present invention, the expression "increase of photographic speed with respect to lightsensitive materials" means that the value  $S_{0.2}$  is increased by 0.02 or more, preferably 0.03 or more, and more preferably 0.04 or more. The value  $S_{0.2}$  refers to the logarithm of inverse number of exposure intensity required for realizing a density of fog + 0.2 with respect to lightsensitive materials having been developed according to the development processing procedure described in Example 1. The compound capable of increasing photographic speed refers to a compound which causes the  $S_{0.2}$  value of a lightsensitive material containing the compound to be 0.02 or more higher than that of the lightsensitive material not containing the compound.

The compound of the present invention, although

may be used in any of silver halide lightsensitive layers and nonsensitive layers of a lightsensitive material, is preferably used in silver halide lightsensitive layers.

5           When the compound of the present invention is used in two or more silver halide lightsensitive layers whose sensitivities are different from each other, although the compound may be incorporated in layers of any sensitivity, it is preferred that the compound be  
10           incorporated in the layer of the highest sensitivity.

          When the compound of the present invention is used in a nonsensitive layer, it is preferred that the compound be incorporated in an interlayer disposed between a red-sensitive layer and a green-sensitive  
15           layer or between a green-sensitive layer and a blue-sensitive layer.

          Although the method of introducing the compound of the present invention in a lightsensitive material is not particularly limited and use can be made of, for  
20           example, any of the method of emulsifying the compound together with a high-boiling organic solvent, etc., the method of solid dispersion, the method of dissolving the compound in an organic solvent such as methanol and adding the solution to coating liquids and the method  
25           of adding the compound at the time of preparation of silver halide emulsions, it is preferred to introduce the compound in a lightsensitive material through

emulsification.

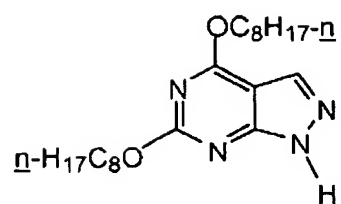
The compounds of the present invention comprehend a compound that reacts with developing agent oxidation products to thereby release residues of the compound having at least three heteroatoms, which compound can preferably be employed.

The content of compound of the present invention, although not particularly limited, is preferably in the range of 0.1 to 1000 mg/m<sup>2</sup>, more preferably 1 to 500 mg/m<sup>2</sup>, and most preferably 5 to 100 mg/m<sup>2</sup> of lightsensitive material.

In the use of the compound of the present invention in lightsensitive silver halide emulsion layers, the content thereof per layer is preferably in the range of  $1 \times 10^{-4}$  to  $1 \times 10^{-1}$  mol, more preferably  $1 \times 10^{-3}$  to  $5 \times 10^{-2}$  mol per mol of silver.

Specific examples of the compounds of the present invention will be shown below, which however in no way limit the scope of compounds according to the present invention.

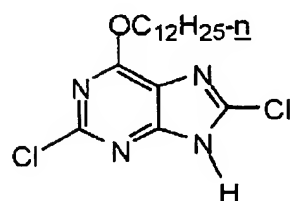
HET-1



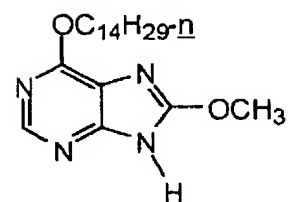
HET-6



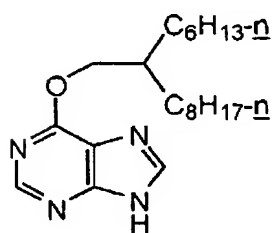
HET-2



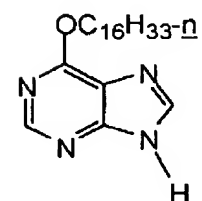
HET-7



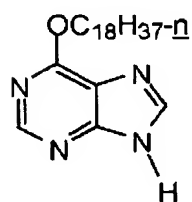
HET-3



HET-8



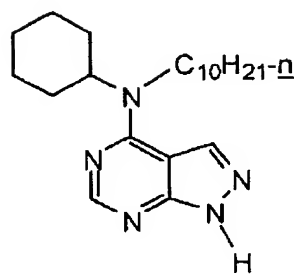
HET-4



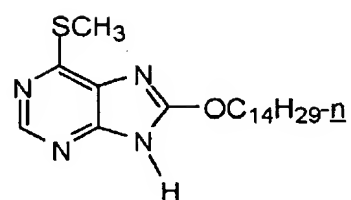
HET-9



HET-5



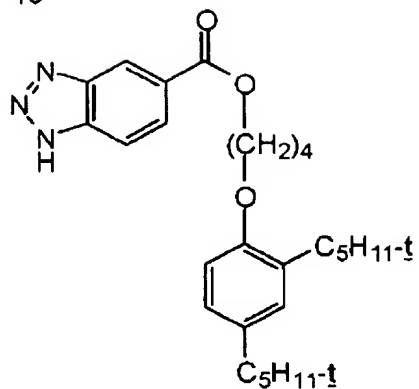
HET-10



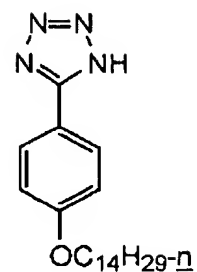


CCCCC(C(=O)Nc1ccc(Oc2nc3nc[nH]3n2)cc1)Oc4ccc(S(=O)(=O)CCCCCCCCCCCCCCCC)cc4CCCCCc1ccc(cc1)Oc2c(C)oc(=O)c3nc4ncnc4n3O=C1C(=N2C(=N1)N(C2)c3ccccc3)OC10H21-11C1=NC2=C(N1)N=CN=C2SC(C)(C)C3=CC=CC=C3COC1=NC2=C(N1)N=CN=C2SC12H25[H]N1=NN=C2C(=C1)C(=CC=C2)OC18H37CCCCCc1ccc(OCC(=O)Nc2ccccc2N3N=NN=C3S)cc1CCCCCS1=NC2=C(N1)N=CN=C2C3=NC(=N3)C4CCCCCCCCCCCC4

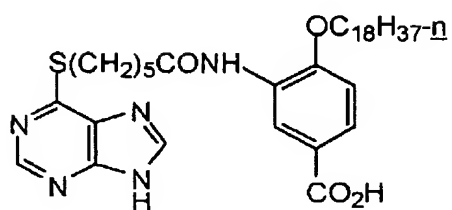
HET-19



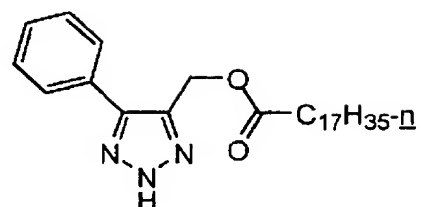
HET-23



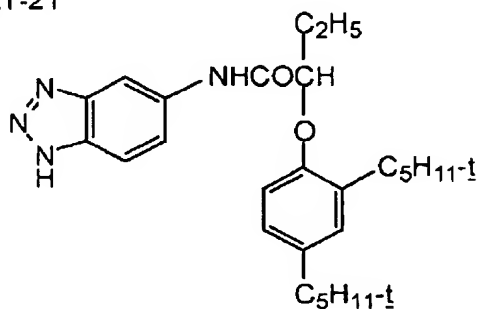
HET-20



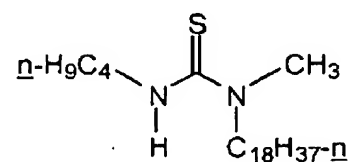
HET-24



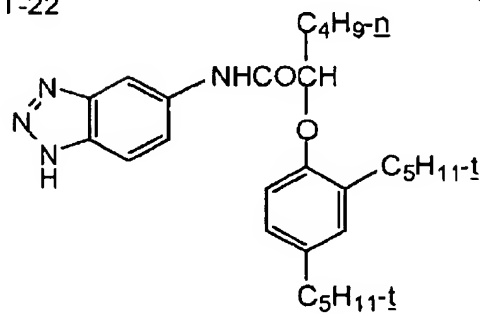
HET-21



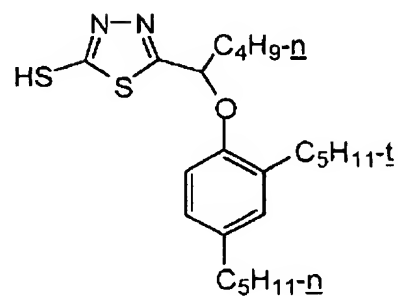
HET-25



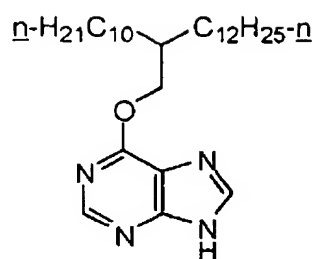
HET-22



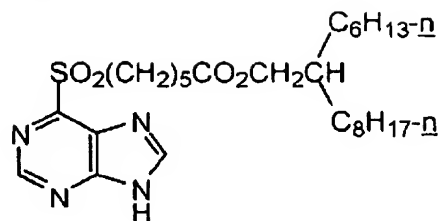
HET-26



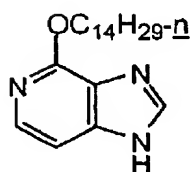
HET-27



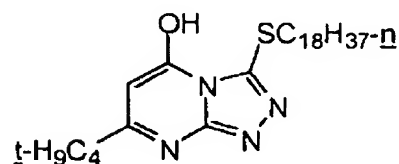
HET-32



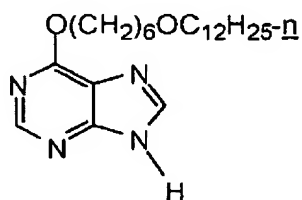
HET-28



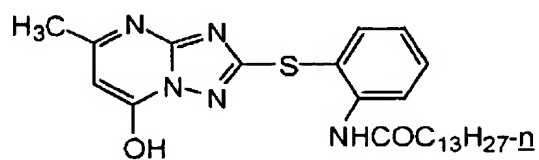
HET-33



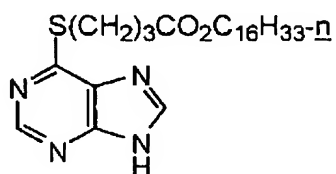
HET-29



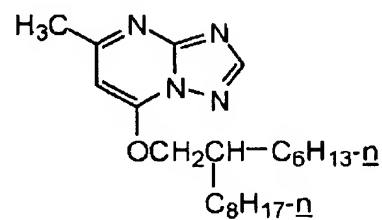
HET-34



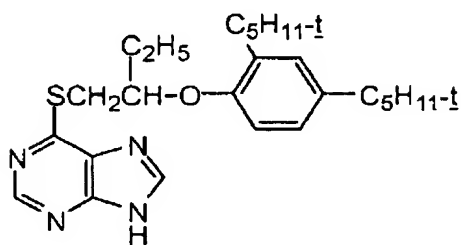
HET-30



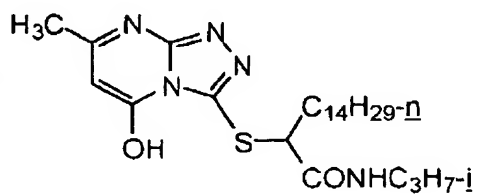
HET-35



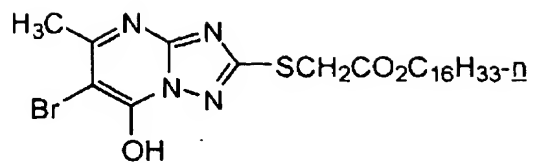
HET-31



HET-36

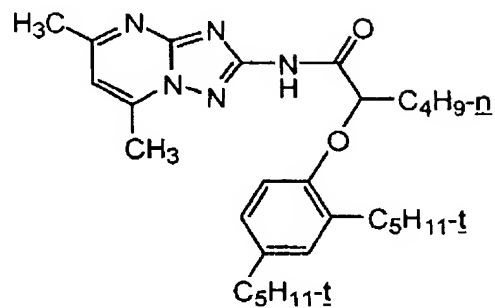
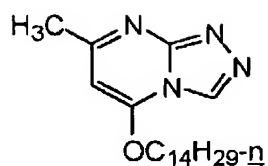


HET-37

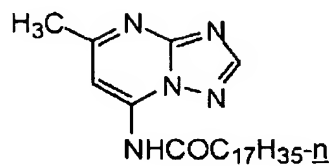


HET-41

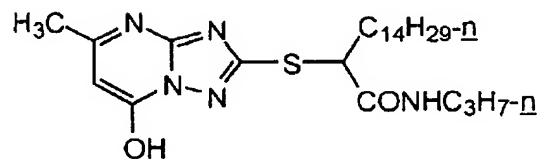
HET-38



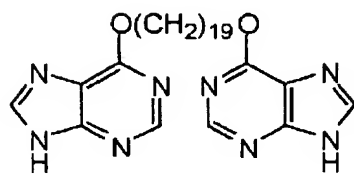
HET-39



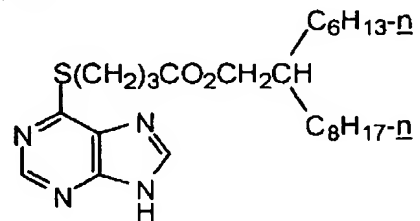
HET-42



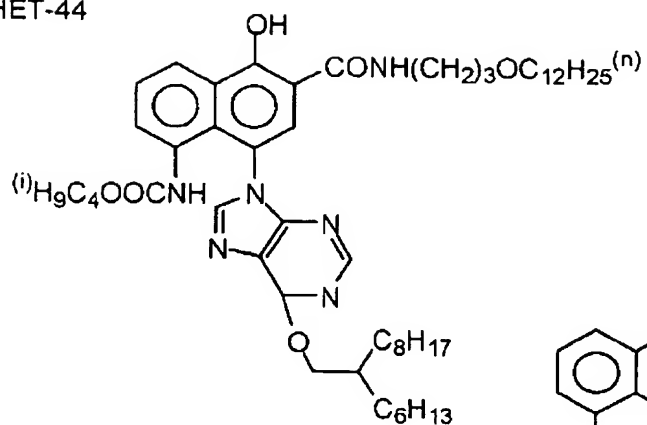
HET-40



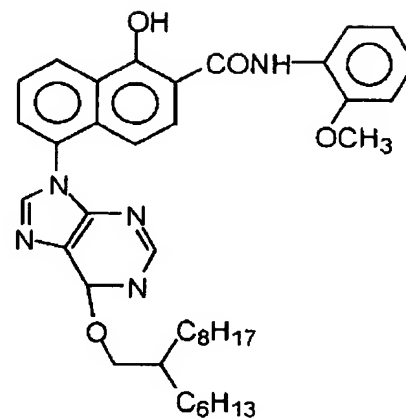
HET-43



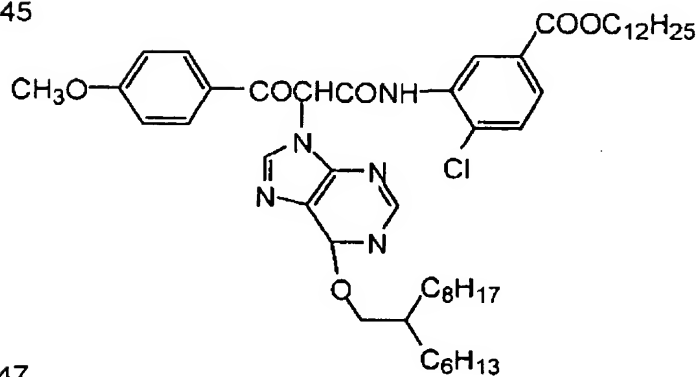
HET-44



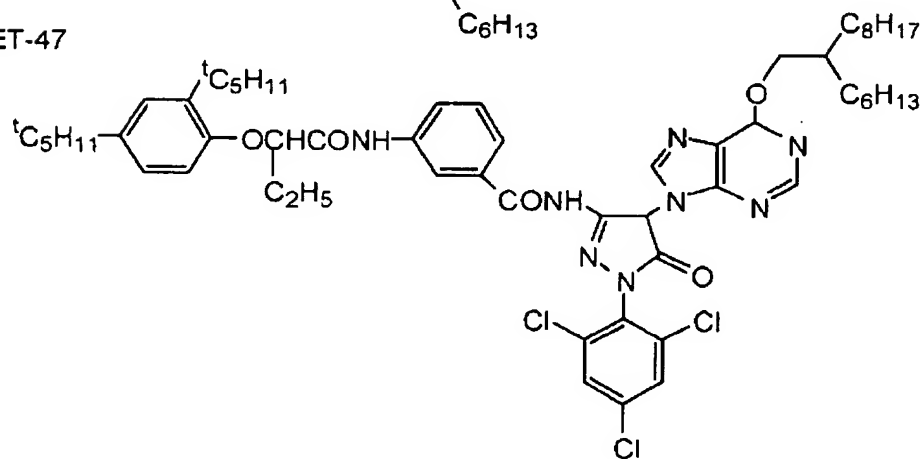
HET-46



HET-45

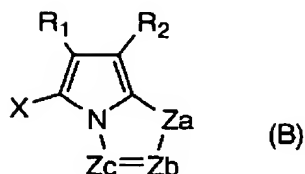
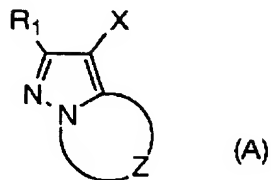


HET-47



Now, the compounds of the general formula (A) or general formula (B) that can preferably be used in the

present invention will be described.



5

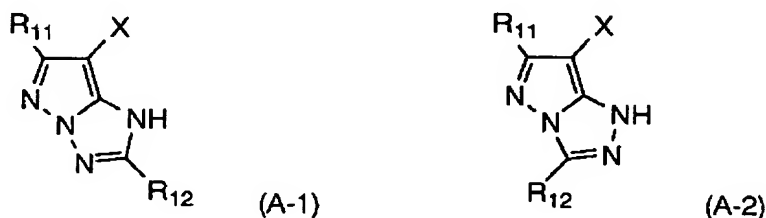
In the general formula (A),  $R_1$  represents a hydrogen atom or a substituent.  $Z$  represents a nonmetallic atom group required for forming a 5-membered azole ring containing 2 to 4 nitrogen atoms. The azole ring may have a substituent (including a condensed ring).  $X$  represents a hydrogen atom or a substituent.

In the general formula (B),  $Z_a$  represents  $-NH-$  or  $-CH(R_3)-$ . Each of  $Z_b$  and  $Z_c$  independently represents  $-C(R_4)=$  or  $-N=$ . Each of  $R_1$ ,  $R_2$  and  $R_3$  independently represents an electron withdrawing group whose Hammett substituent constant  $\sigma_p$  value is in the range of 0.2 to 1.0.  $R_4$  represents a hydrogen atom or a substituent, provided that when there are two  $R_4$ s in the formula, the two  $R_4$ s may be identical with or different from each other.  $X$  represents a hydrogen atom or a substituent.

These compounds will be described in detail below. Among the skeletons represented by the general

formula (A), those preferred are 1H-pyrazolo[1,5-b][1,2,4]triazole and 1H-pyrazolo[5,1-c][1,2,4]triazole, which are represented by the general formula (A-1) and general formula (A-2), respectively.

5



In the formulae, each of R<sub>11</sub> and R<sub>12</sub> represents a substituent. X represents a hydrogen atom or a substituent.

10

The substituents R<sub>11</sub>, R<sub>12</sub> and X of the general formulae (A-1) and (A-2) will be described in detail below.

15

As the substituent R<sub>11</sub>, there can be mentioned, for example, a halogen atom (e.g., a chlorine atom, a bromine atom or a fluorine atom); an alkyl group (having 1 to 60 carbon atoms, such as methyl, ethyl, propyl, isobutyl, t-butyl, t-octyl, 1-ethylhexyl, nonyl, undecyl, pentadecyl, n-hexadecyl or 3-decanamidopropyl); an alkenyl group (having 2 to 60 carbon atoms, such as vinyl, allyl or oleyl); a cycloalkyl group (having 5 to 60 carbon atoms, such as cyclopentyl, cyclohexyl, 4-t-butylcyclohexyl, 1-indenyl or cyclododecyl); an aryl group (having 6 to 60 carbon atoms, such as phenyl, p-tolyl or naphthyl); an

20

acylamino group (having 2 to 60 carbon atoms, such as acetylamino, n-butanamido, octanoylamino, 2-hexyldecanamido, 2-(2',4'-di-t-amylphenoxy)butanamido, benzoylamino or nicotinamido); a sulfonamido group  
5 (having 1 to 60 carbon atoms, such as methanesulfonamido, octanesulfonamido or benzenesulfonamido); a ureido group (having 2 to 60 carbon atoms, such as decylaminocarbonylamino or di-n-octylaminocarbonylamino); a urethane group (having  
10 2 to 60 carbon atoms, such as dodecyloxycarbonylamino, phoxycarbonylamino or 2-ethylhexyloxycarbonylamino); an alkoxy group (having 1 to 60 carbon atoms, such as methoxy, ethoxy, butoxy, n-octyloxy, hexadecyloxy or methoxyethoxy); an aryloxy group (having 6 to 60 carbon  
15 atoms, such as phenoxy, 2,4-di-t-amylphenoxy, 4-t-octylphenoxy or naphthoxy); an alkylthio group (having 1 to 60 carbon atoms, such as methylthio, ethylthio, butylthio or hexadecylthio); an arylthio group (having 6 to 60 carbon atoms, such as phenylthio or 4-  
20 dodecyloxyphenylthio); an acyl group (having 1 to 60 carbon atoms, such as acetyl, benzoyl, butanoyl or dodecanoyl); a sulfonyl group (having 1 to 60 carbon atoms, such as methanesulfonyl, butanesulfonyl or toluenesulfonyl); a cyano group; a carbamoyl group  
25 (having 1 to 60 carbon atoms, such as N,N-dicyclohexylcarbamoyl); a sulfamoyl group (having 0 to 60 carbon atoms, such as N,N-dimethylsulfamoyl); a



hydroxyl group; a sulfo group; a carboxyl group; a  
nitro group; an alkylamino group (having 1 to 60 carbon  
atoms, such as methylamino, diethylamino, octylamino or  
octadecylamino); an arylamino group (having 6 to  
5 60 carbon atoms, such as phenylamino, naphthylaminor or  
N-methyl-N-phenylamino); a heterocyclic group (having 0  
to 60 carbon atoms, preferably heterocyclic group  
wherein an atom selected from among a nitrogen atom, an  
oxygen atom and a sulfur atom is used as a heteroatom  
10 being a constituent of the ring, more preferably  
heterocyclic group wherein not only a heteroatom but  
also a carbon atom is used as constituent atoms of the  
ring, especially heterocyclic group having a 3 to 8-,  
preferably 5 to 6-membered ring, such as heterocyclic  
15 groups listed later with respect to the substituent X);  
an acyloxy group (having 1 to 60 carbon atoms, such as  
formyloxy, acetyloxy, myristoyloxy or benzoyloxy); or  
the like.

Among these groups, the alkyl, cycloalkyl, aryl,  
20 acylamino, ureido, urethane, alkoxy, aryloxy,  
alkylthio, arylthio, acyl, sulfonyl, cyano, carbamoyl  
and sulfamoyl groups include those having substituents  
and those, if practicable, having condensed rings.  
Examples of such substituents include an alkyl group, a  
25 cycloalkyl group, an aryl group, an acylamino group, a  
ureido group, a urethane group, an alkoxy group, an  
aryloxy group, an alkylthio group, an arylthio group,

an acyl group, a sulfonyl group, a cyano group, a carbamoyl group and a sulfamoyl group. As the condensed rings, there can be mentioned benzene and the like.

5           Among these substituents, an alkyl group, an aryl group, an alkoxy group or an aryloxy group can be mentioned as preferred  $R_{11}$ . An alkyl group, an alkoxy group or an aryloxy group can be mentioned as more preferred  $R_{11}$ . The most preferred  $R_{11}$  is a branched  
10 alkyl group.

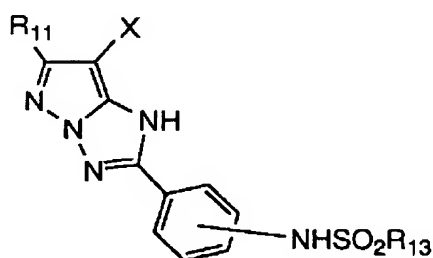
          X represents a hydrogen atom or a substituent. This substituent can be any of the substituents listed as  $R_{11}$  above. The substituent represented by X is preferably an alkyl group, an alkoxycarbonyl group, a  
15 carbamoyl group or a group split off at the reaction with developing agent oxidation products. As this group, there can be mentioned, for example, a halogen atom (e.g., a fluorine atom, a chlorine atom or a bromine atom); an alkoxy group (e.g., ethoxy,  
20 methoxycarbonylmethoxy, carboxypropyloxy, methanesulfonylethoxy or perfluoropropoxy); an aryloxy group (e.g., 4-carboxyphenoxy, 4-(4-hydroxyphenylsulfonyl)phenoxy, 4-methanesulfonyl-3-carboxyphenoxy or 2-methanesulfonyl-4-acetylsulfamoylphenoxy); an acyloxy group (e.g.,  
25 acetoxo or benzoyloxy); a sulfonyloxy group (e.g., methanesulfonyloxy or benzenesulfonyloxy); an acylamino

group (e.g., heptafluorobutyrylamino); a sulfonamido group (e.g., methanesulfonamido); an alkoxycarbonyloxy group (e.g., ethoxycarbonyloxy); a carbamoyloxy group (e.g., diethylcarbamoyloxy, piperidinocarbonyloxy or morpholinocarbonyloxy); an alkylthio group (e.g., 2-carboxyethylthio); an arylthio group (e.g., 2-octyloxy-5-t-octylphenylthio or 2-(2,4-di-t-  
5 amylphenoxy)butyrylamino-phenylthio); a heterocyclic thio group (e.g., 1-phenyltetrazolylthio or 2-  
10 benzimidazolylthio); a heterocyclic oxy group (e.g., 2-pyridyloxy or 5-nitro-2-pyridyloxy); a 5- or 6-membered nitrogenous heterocyclic group (e.g., 1-triazolyl, 1-imidazolyl, 1-pyrazolyl, 5-chloro-1-tetrazolyl, 1-benzotriazolyl, 2-phenylcarbamoyl-1-imidazolyl, 5,5-  
15 dimethylhydantoin-3-yl, 1-benzylhydantoin-3-yl, 5,5-dimethylloxazolidine-2,4-dione-3-yl or purine); or an azo group (e.g., 4-methoxyphenylazo or 4-pivaloylamino-phenylazo).

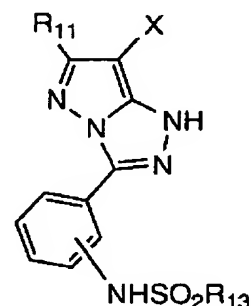
The substituent represented by X is preferably an  
20 alkyl group, an alkoxycarbonyl group, a carbamoyl group, a halogen atom, an alkoxy group, an aryloxy group, an alkyl- or arylthio group or a 5- or 6-membered nitrogenous heterocyclic group having coupling-active nitrogen atom bonding. The substituent  
25 is more preferably an alkyl group, a carbamoyl group, a halogen atom, a substituted aryloxy group, a substituted arylthio group, an alkylthio group or a

1-pyrazolyl group.

The substituent represented by  $R_{12}$  can be the same as listed with respect to  $R_{11}$ . The substituent represented by  $R_{12}$  is preferably an alkyl group, an aryl group, a heterocyclic group, an alkoxy group or an aryloxy group. The substituent is more preferably a substituted alkyl group or a substituted aryl group, and is most preferably a substituted aryl group. Compounds of the general formulae (A-3) and (A-4) are preferred. In the general formulae (A-3) and (A-4), the position of  $-NHSO_2R_{13}$  substitution, although not particularly limited, is preferably m- or p- position, most preferably p- position.



(A-3)



(A-4)

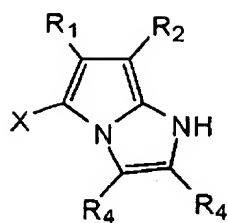
In the general formulae,  $R_{11}$  and  $X$  are as defined above with respect to the general formulae (A-1) and (A-2), and  $R_{13}$  represents a substituent. The substituent represented by  $R_{13}$  can be any of those listed as  $R_{11}$  above. The substituent represented by  $R_{13}$  is preferably a substituted aryl group or a substituted or unsubstituted alkyl group. This

substituent can be any of those listed as  $R_{11}$  above.

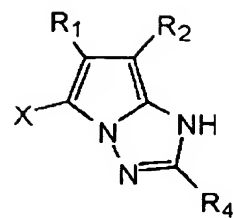
The compounds represented by the general formulae (A-1) and (A-2) and preferably employed in the present invention may form a dimer or oligomer through  
5  $R_{11}$  or  $R_{12}$ , or may be bonded to a polymer chain. In the present invention, the compounds of the general formula (A-1) are preferred, and the compounds of the general formula (A-3) are more preferred.

Now, the general formula (B) will be described.

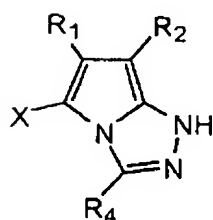
10 Examples of the compounds represented by the general formula (B) according to the present invention include those of the following general formulae (B3) to (B10).



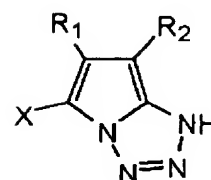
(B3)



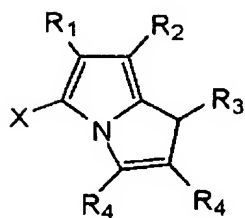
(B4)



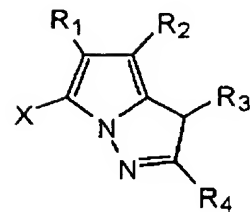
(B5)



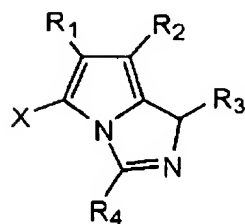
(B6)



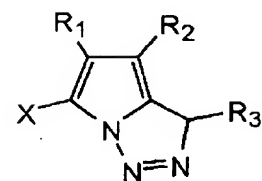
(B7)



(B8)



(B9)



(B10)

In these general formulae, R<sub>1</sub> to R<sub>4</sub> and X have the same meaning as in the general formula (B).

In the present invention, the compounds of the

general formulae (B3), (B4), (B5) and (B8) are preferred, and the compounds of the general formula (B4) are most preferred.

5 In the general formula (B), the substituent represented by  $R_1$ ,  $R_2$  or  $R_3$  is an electron withdrawing group whose Hammett substituent constant  $\sigma_p$  value is in the range of 0.20 to 1.0. Preferably, the  $\sigma_p$  value is in the range of 0.2 to 0.8. Hammett's rule is a rule of thumb advocated by L. P. Hammett in 1935 for  
10 quantitatively considering the effect of substituents on the reaction or equilibrium of benzene derivatives, and the appropriateness thereof is now widely recognized. The substituent constant determined in the Hammett's rule involves  $\sigma_p$  value and  $\sigma_m$  value. These  
15 values can be found in a multiplicity of general publications, and are detailed in, for example, "Lange's Handbook of Chemistry" 12th edition by J. A. Dean, 1979 (Mc Graw-Hill), "Kagaku no Ryoiki" special issue, no. 122, p.p. 96 to 103, 1979 (Nankodo), and  
20 Chemical Review, vol. 91, pp. 165-195, 1991.

Although in the present invention, the substituents  $R_1$ ,  $R_2$  and  $R_3$  are limited by the Hammett substituent constant values, this should not be construed as limitation to only substituents whose  
25 values are known from literature and can be found in the above publications, and should naturally be construed as including substituents whose values, even

if unknown from literature, would be included in stated ranges when measured according to the Hammett's rule.

Examples of the electron withdrawing groups whose  $\sigma_p$  values are in the range of 0.2 to 1.0 include an  
5 acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a cyano group, a nitro group, a dialkylphosphono group, a diarylphosphono group, a diarylphosphinyl group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an  
10 arylsulfonyl group and the like. Groups capable of having further substituents among these substituents may have further substituents as mentioned later with respect to  $R_4$ .

Each of  $R_1$ ,  $R_2$  and  $R_3$  preferably represents  
15 an acyl group, an alkoxycarbonyl group, a cycloalkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a cyano group or a sulfonyl group; and more preferably represents a cyano group, an acyl group, an alkoxycarbonyl group, a cycloalkoxycarbonyl  
20 group, an aryloxycarbonyl group or a carbamoyl group.

In a preferred combination of  $R_1$  and  $R_2$ ,  $R_1$  represents a cyano group while  $R_2$  represents a cycloalkoxycarbonyl group or an alkoxycarbonyl group.

$R_4$  represents a hydrogen atom or a substituent.  
25 This substituent can be any of the substituents listed as  $R_{11}$  above.

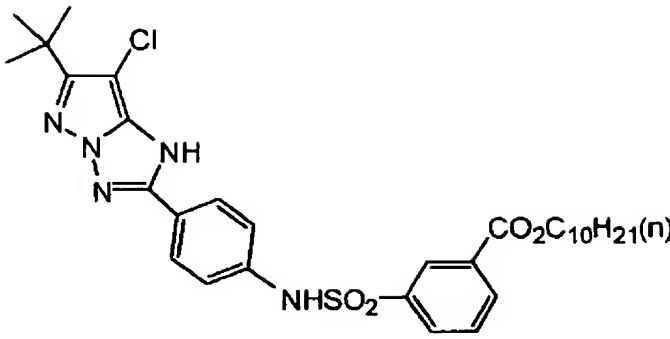
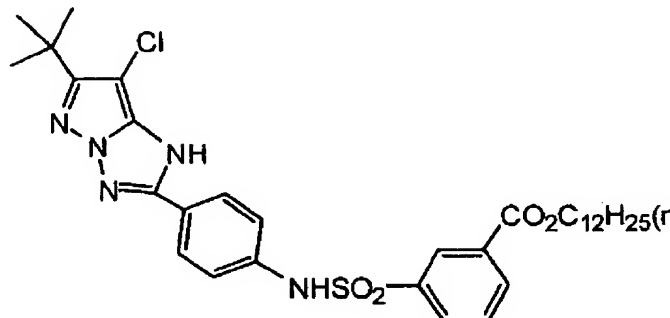
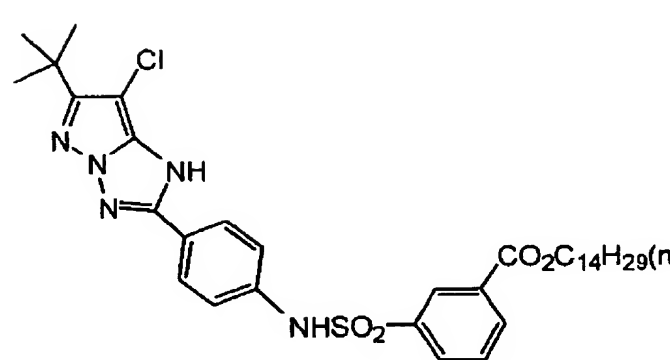
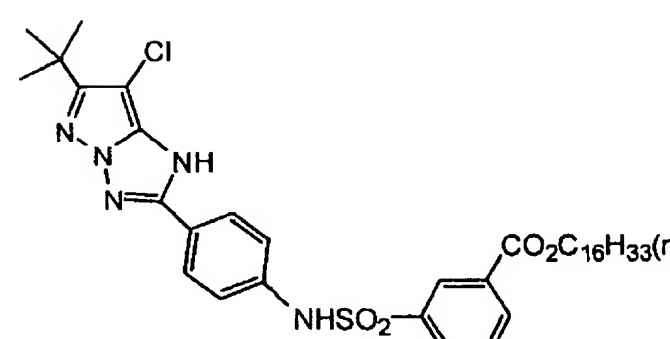
Preferred examples of the substituents represented



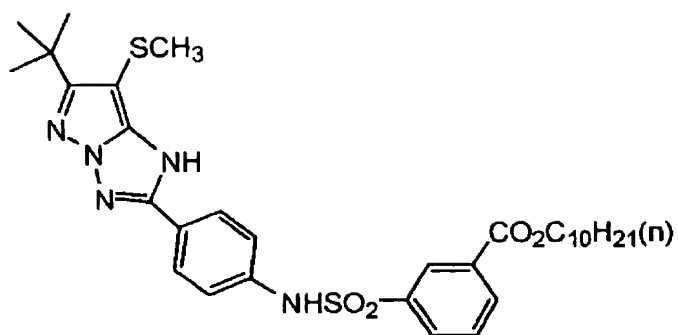
by R<sub>4</sub> include an alkyl group, an aryl group, a  
heterocyclic group, an alkoxy group, an aryloxy group  
and an acylamino group. The substituent represented by  
R<sub>4</sub> is more preferably an alkyl group or a substituted  
5 aryl group, and most preferably a substituted aryl  
group. This substituent can be any of those mentioned  
above.

X has the same meaning as in the general  
formula (A).

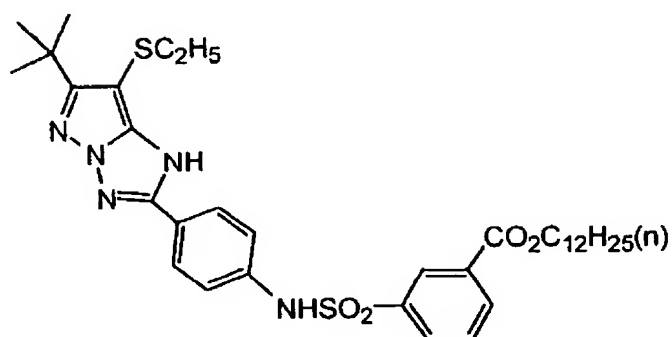
10 Specific examples of the preferably employed  
compounds of the present invention will be shown below,  
which however in no way limit the scope of the present  
invention.

- (1) 
- (2) 
- (3) 
- (4) 

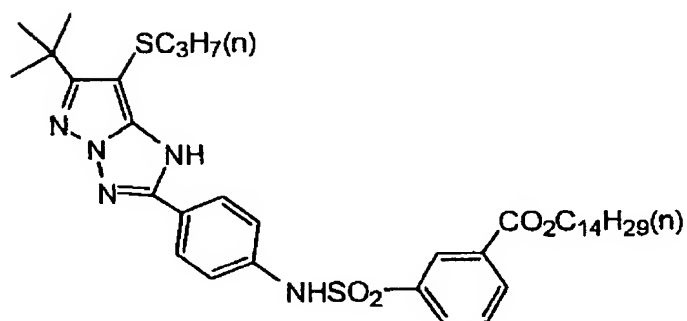
(5)



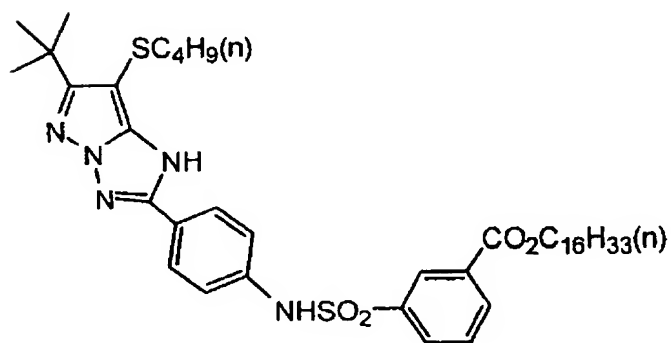
(6)

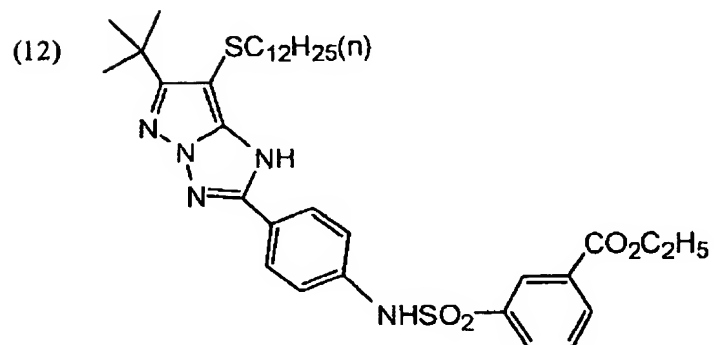
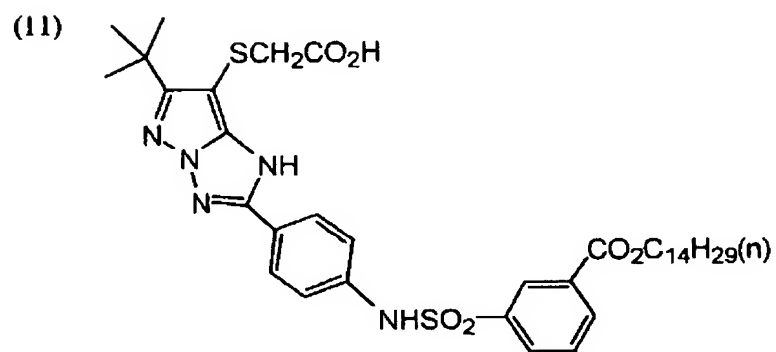
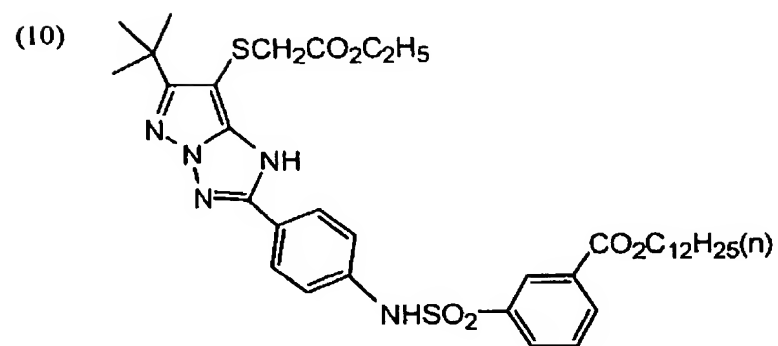
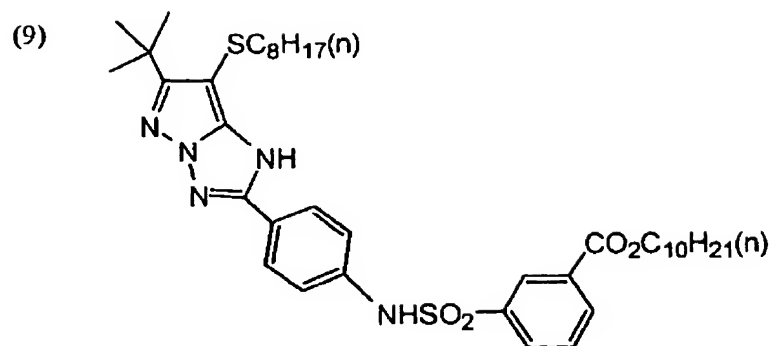


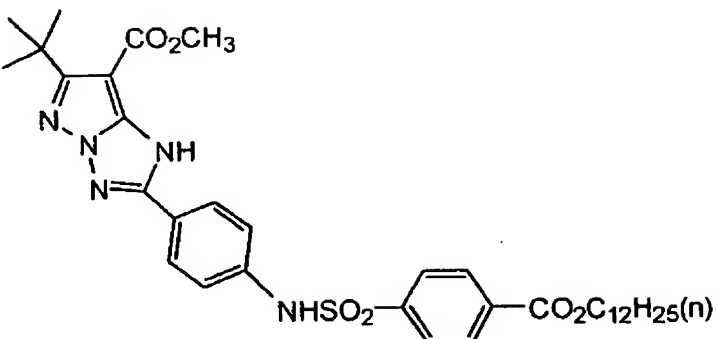
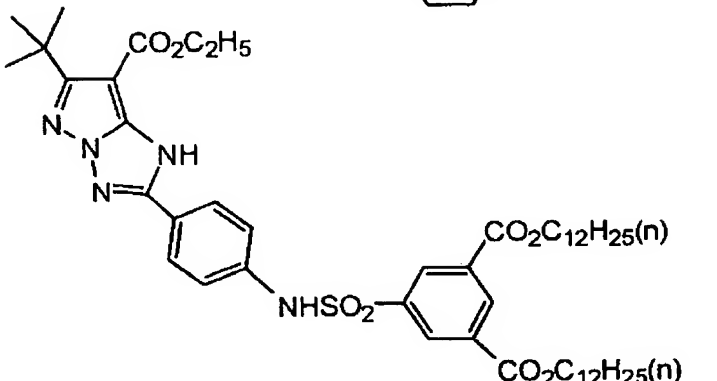
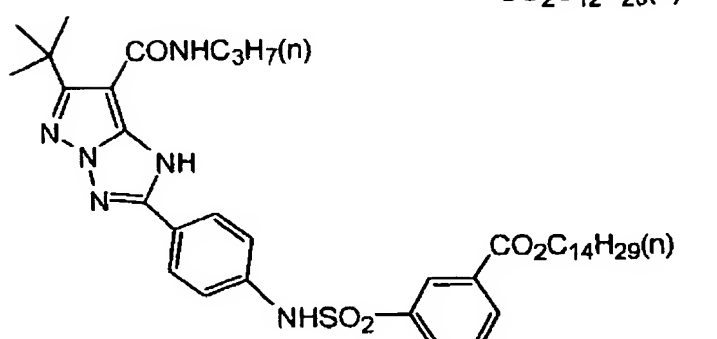
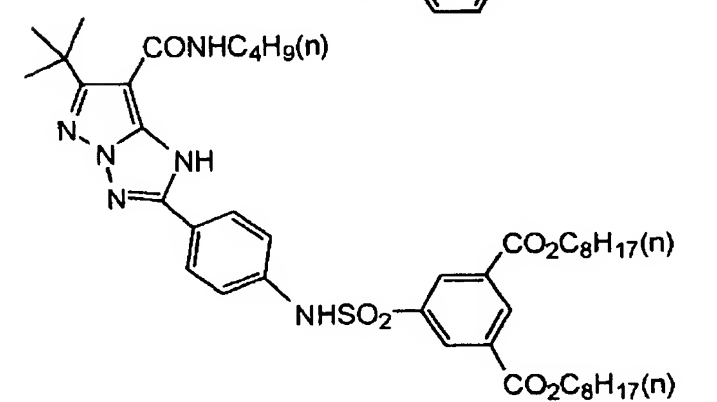
(7)



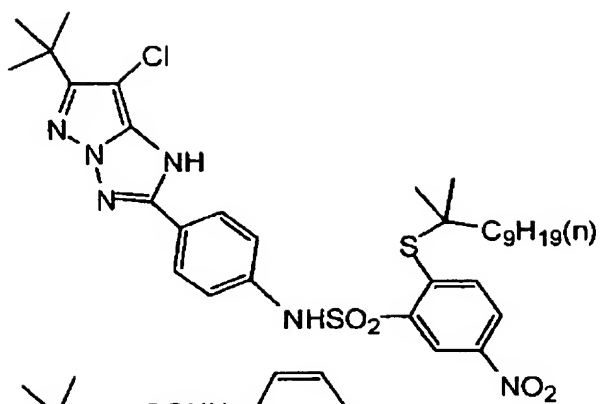
(8)



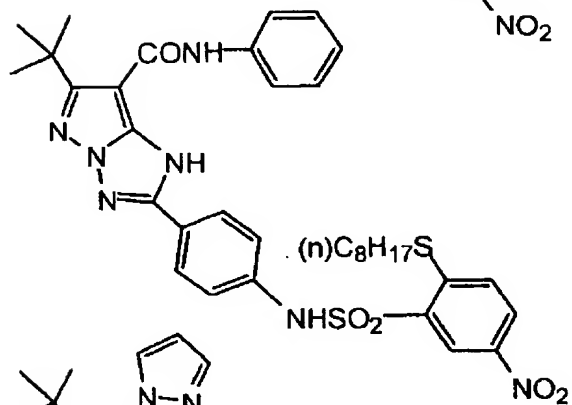


- (13) 
- (14) 
- (15) 
- (16) 

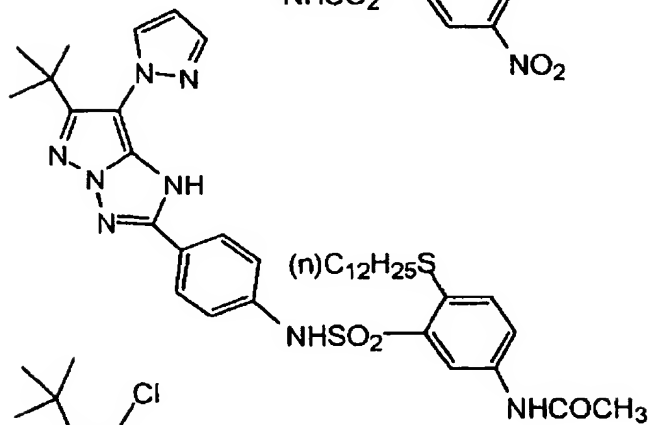
(17)



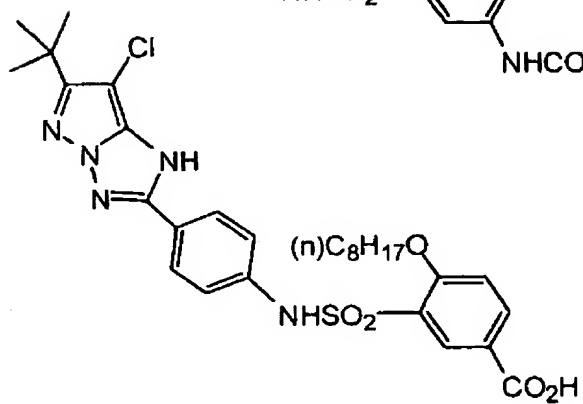
(18)

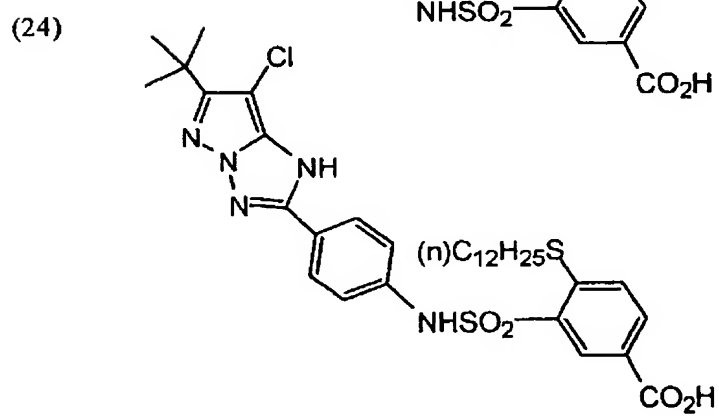
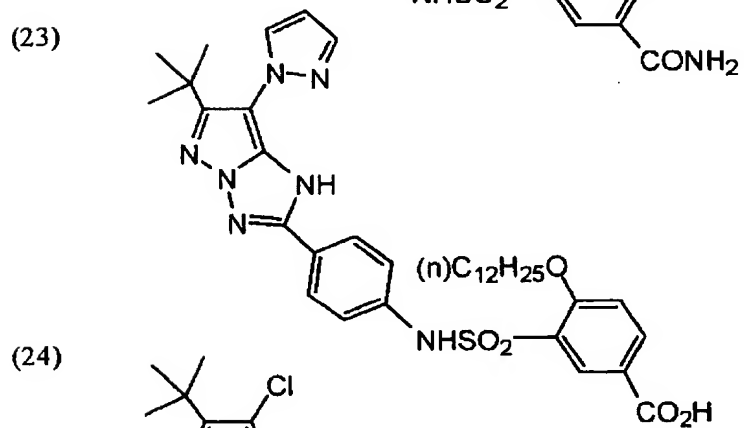
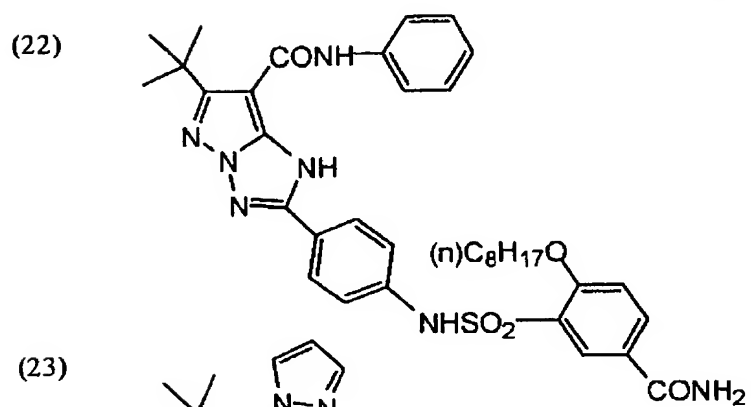
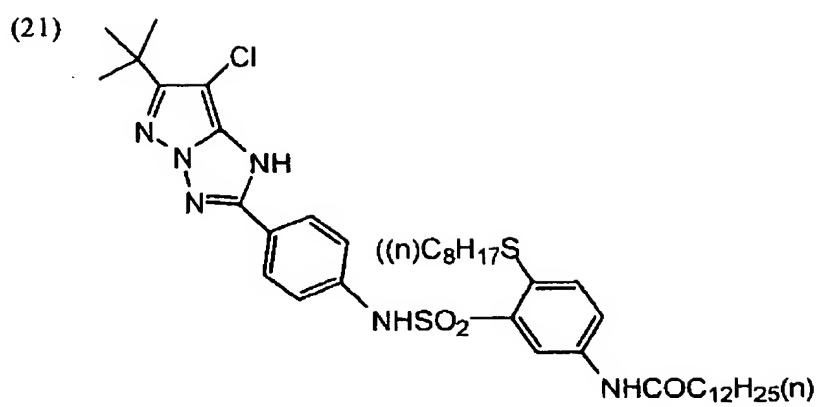


(19)

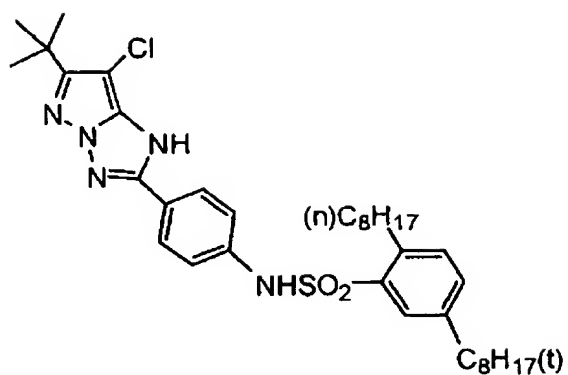


(20)

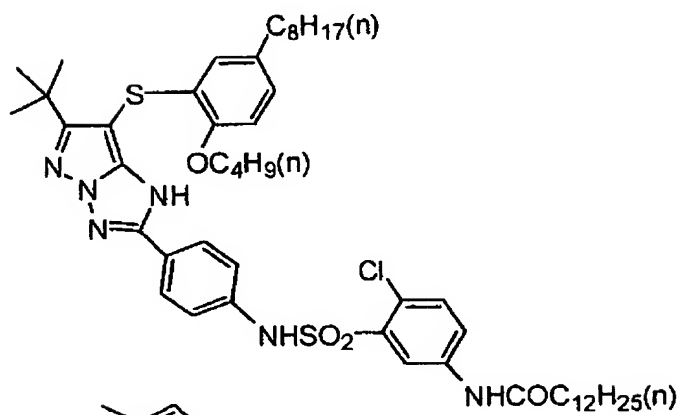




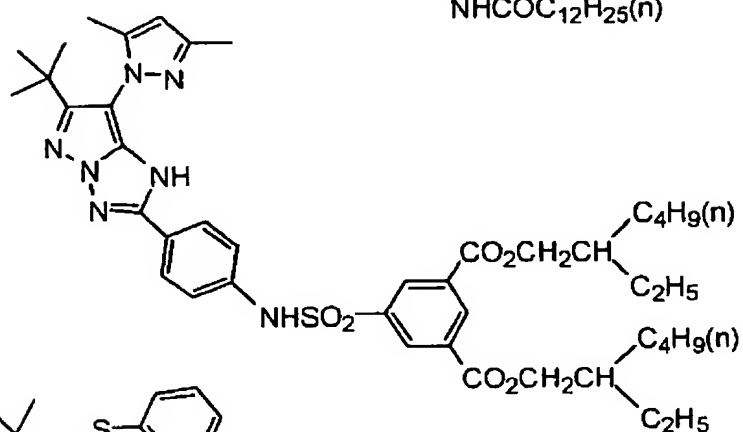
(25)



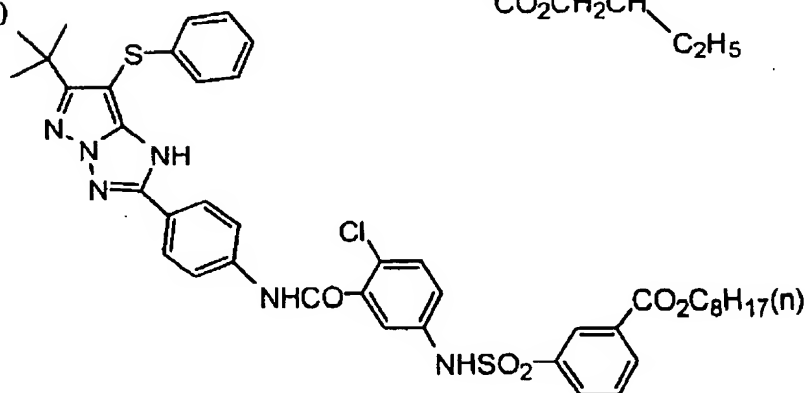
(26)



(27)

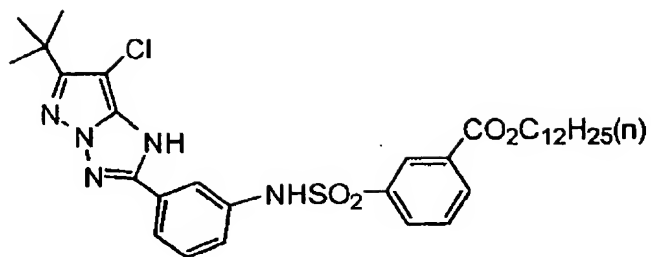


(28)

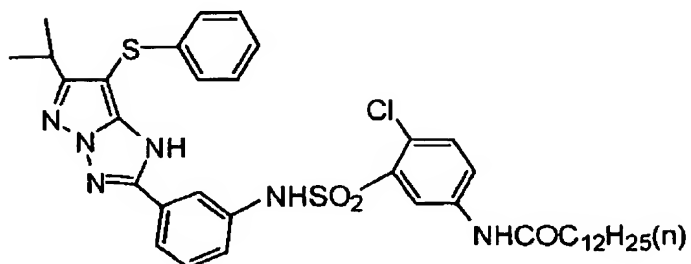




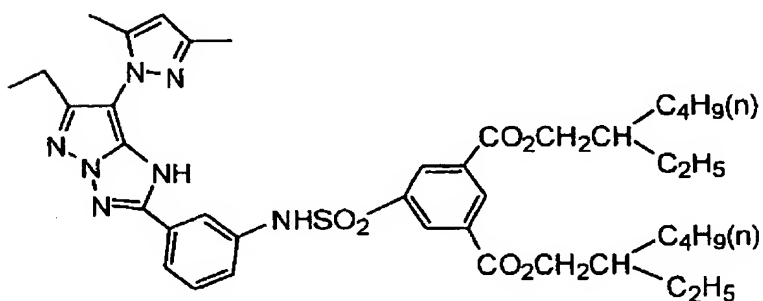
(29)



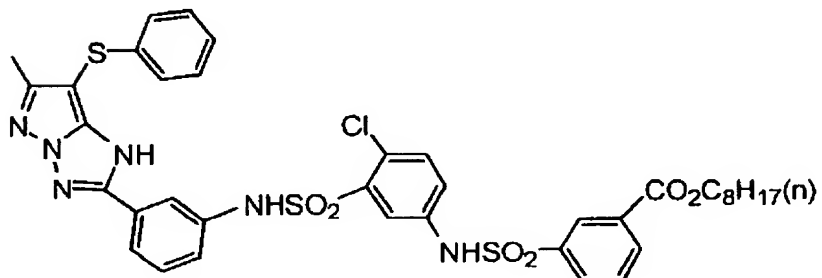
(30)



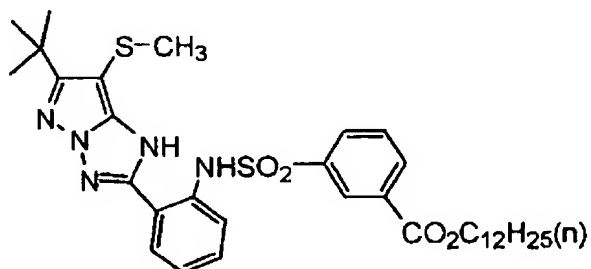
(31)



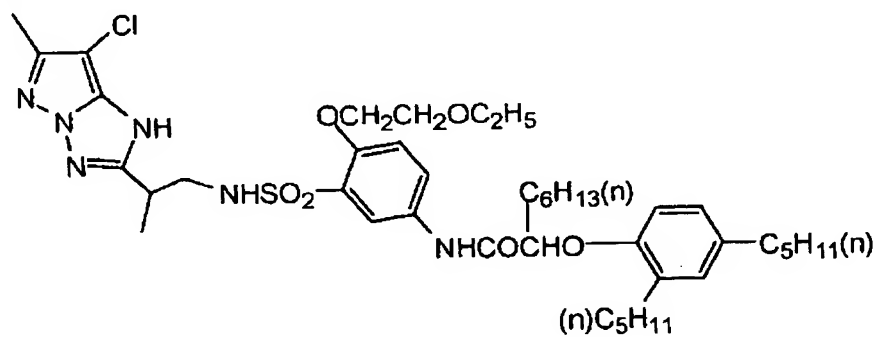
(32)



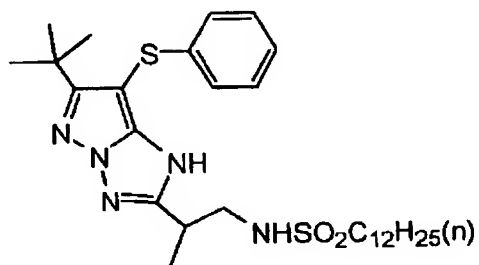
(33)



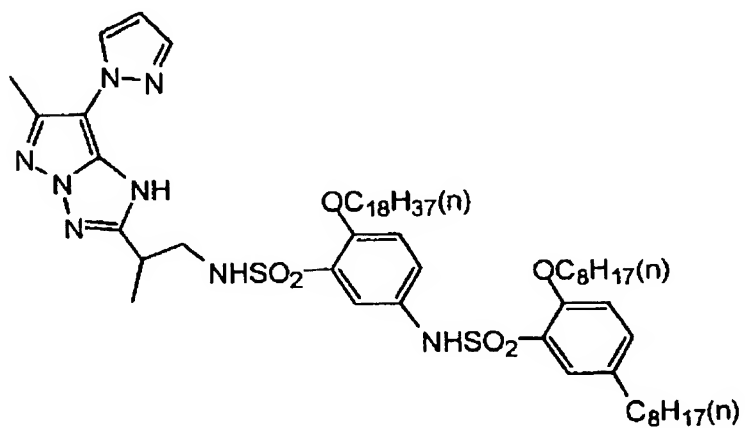
(34)



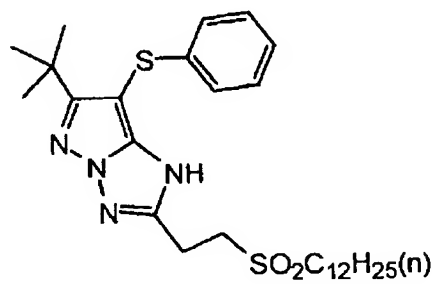
(35)



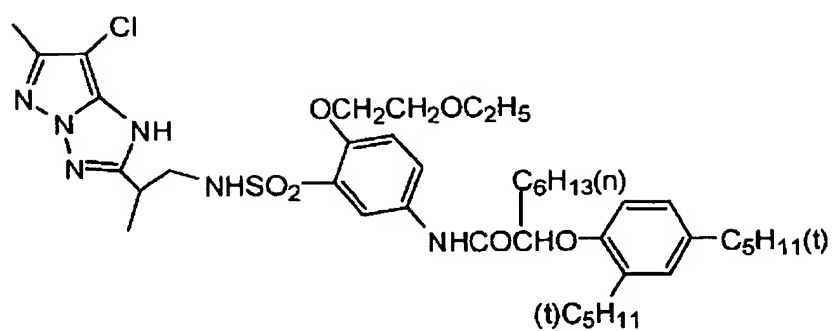
(36)



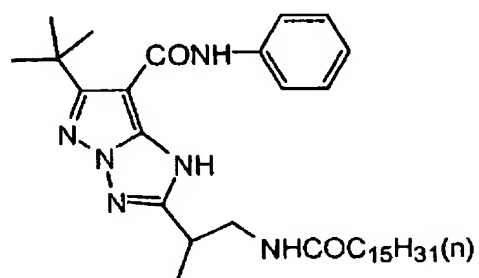
(37)



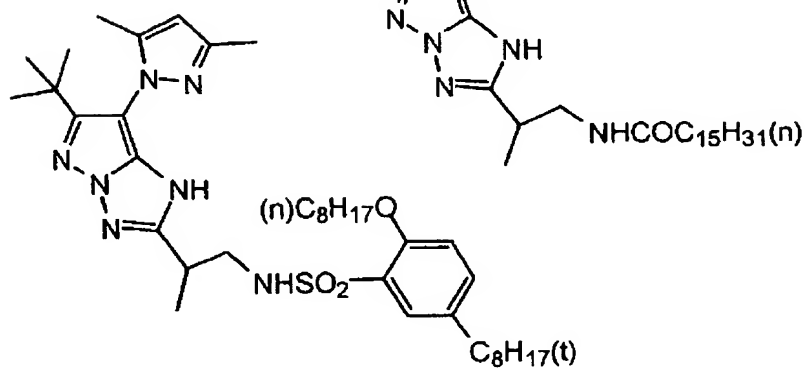
(38)



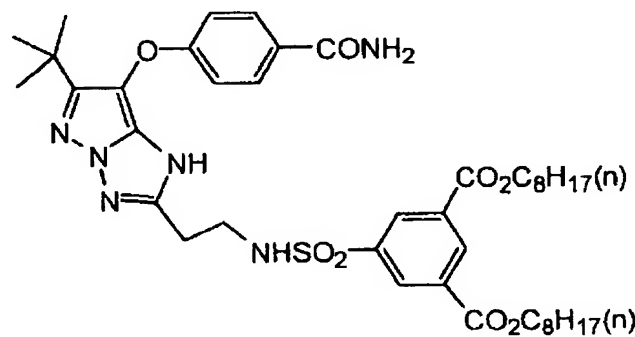
(39)



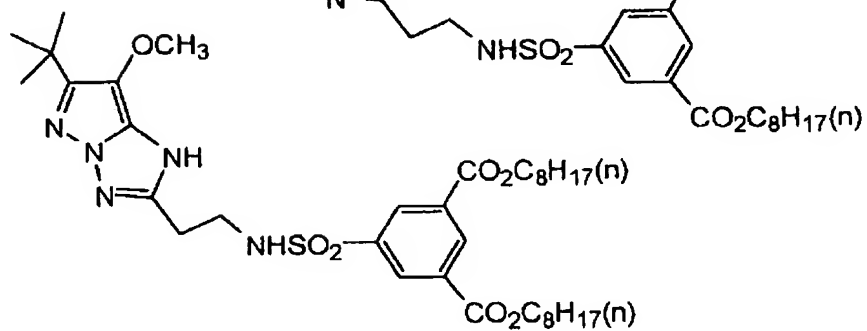
(40)



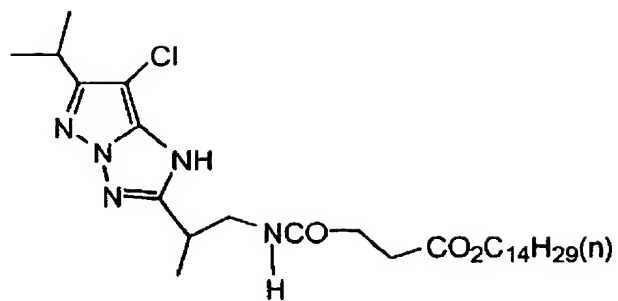
(41)



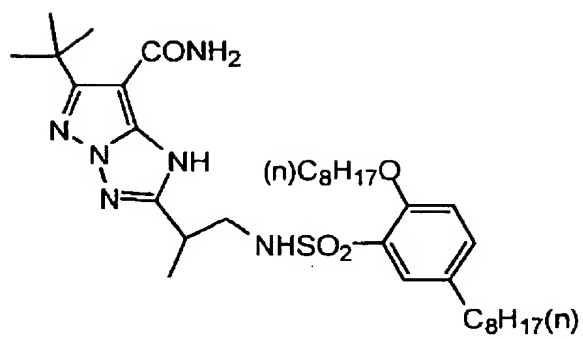
(42)



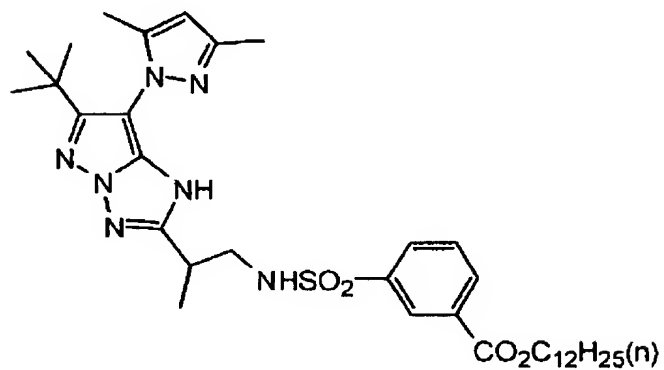
(43)



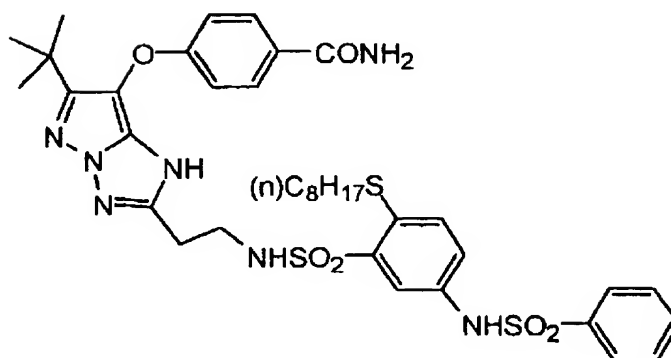
(44)



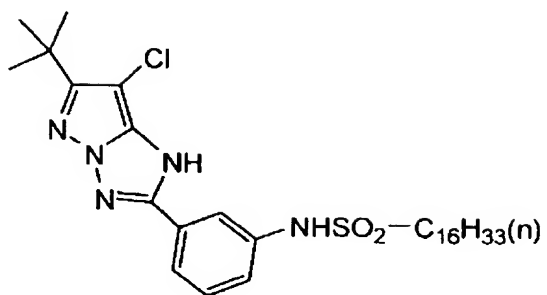
(45)



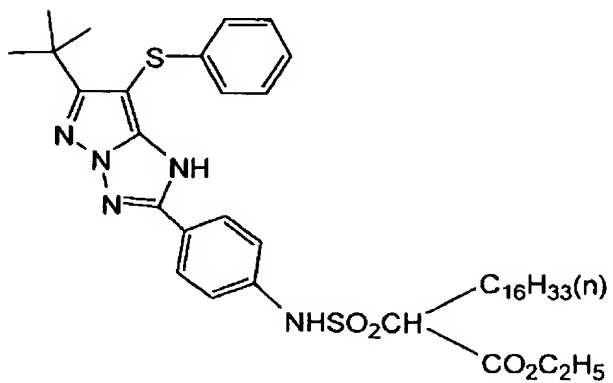
(46)



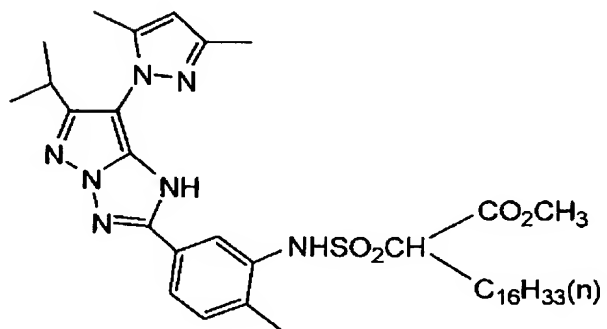
(47)



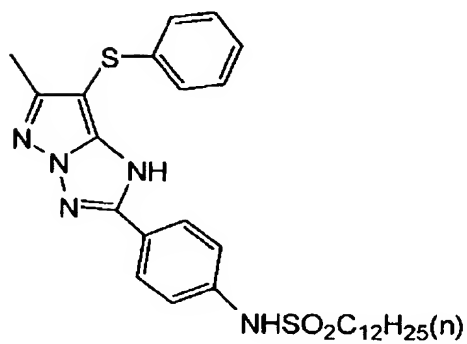
(48)



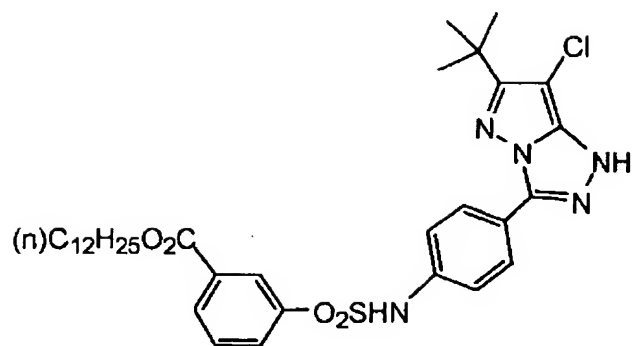
(49)



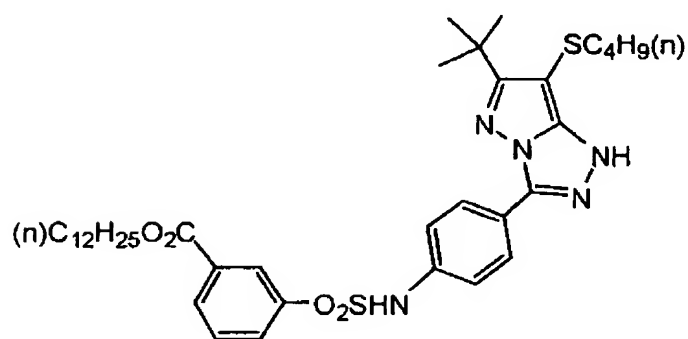
(50)



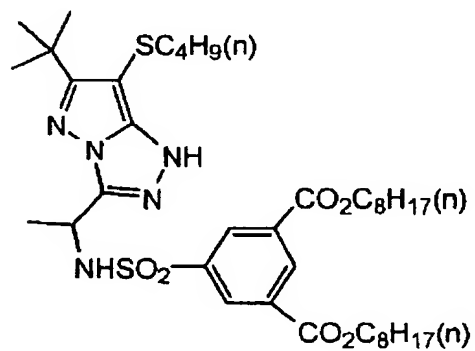
(51)



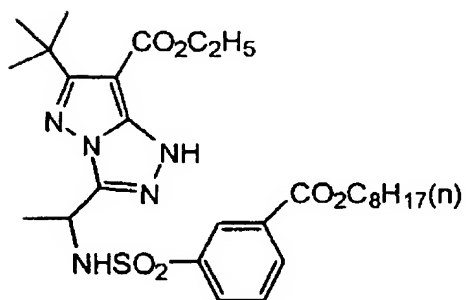
(52)



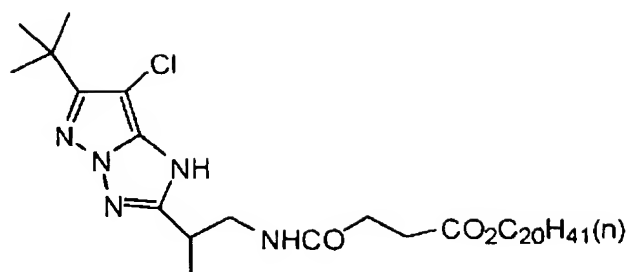
(53)



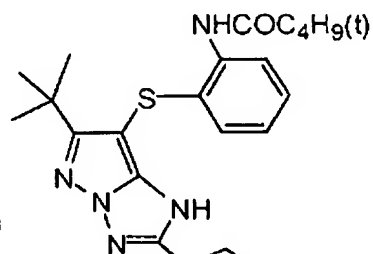
(54)



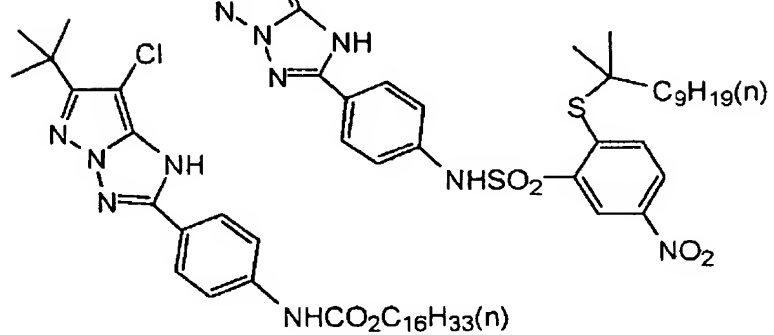
(55)



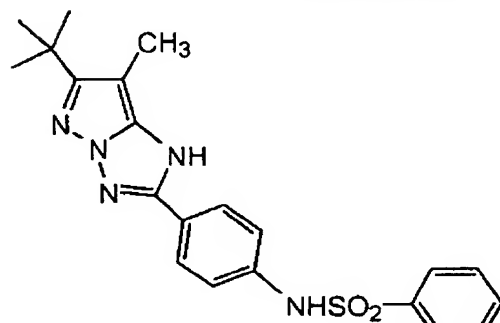
(56)



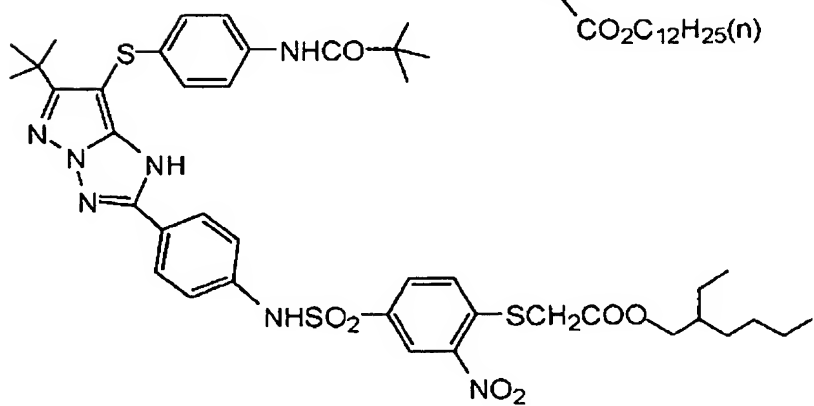
(57)



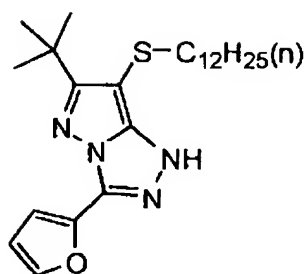
(58)



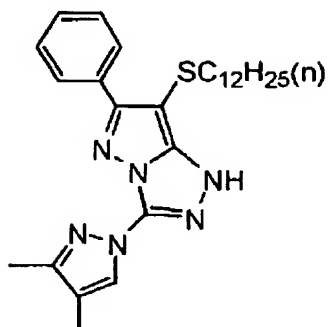
(59)



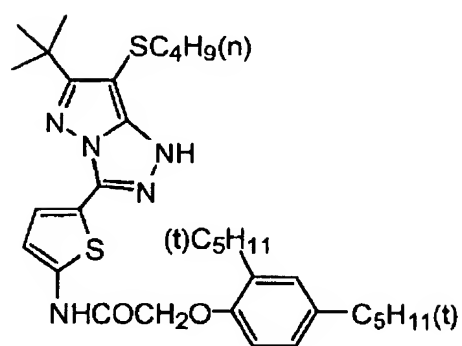
(60)



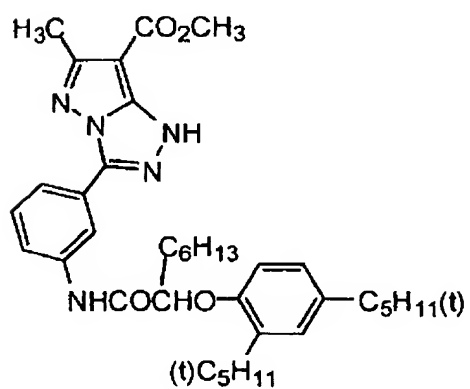
(61)



(62)

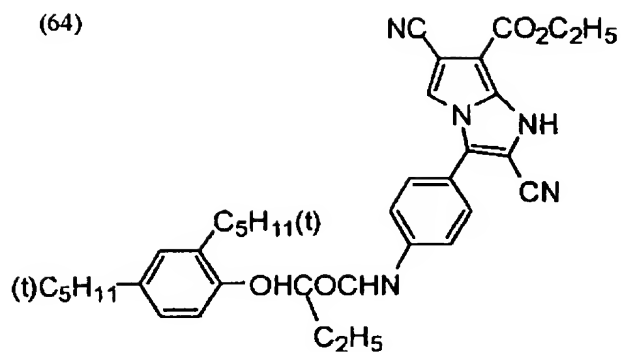


(63)

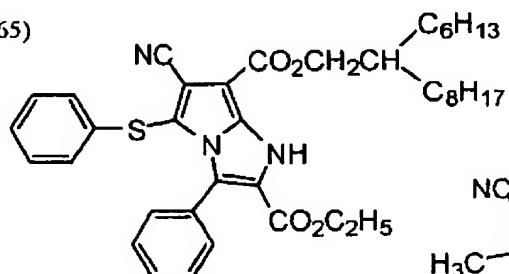




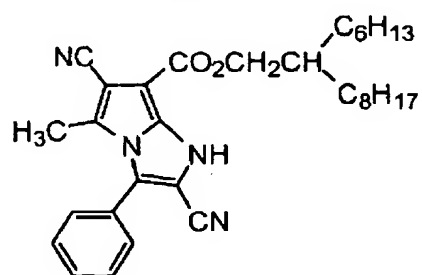
(64)



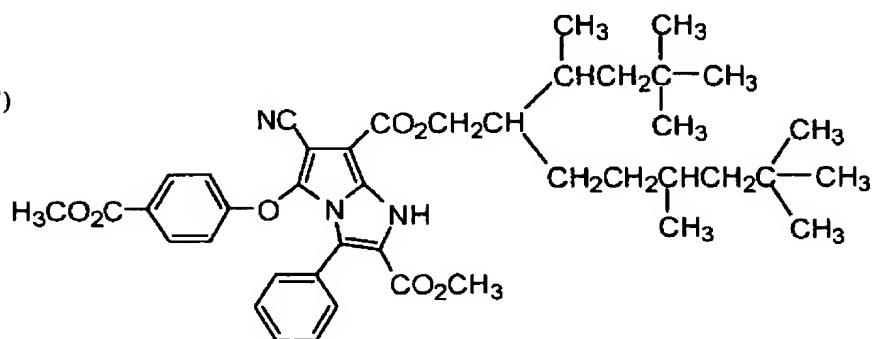
(65)



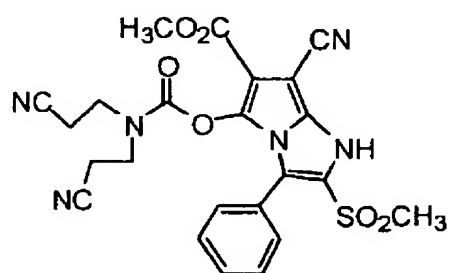
(66)



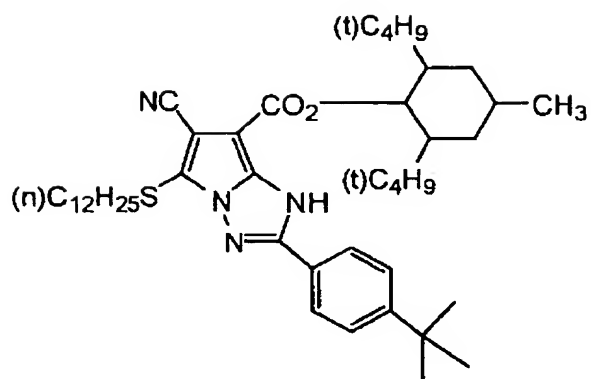
(67)



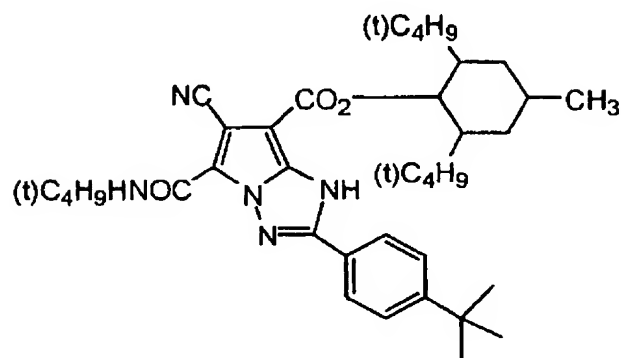
(68)



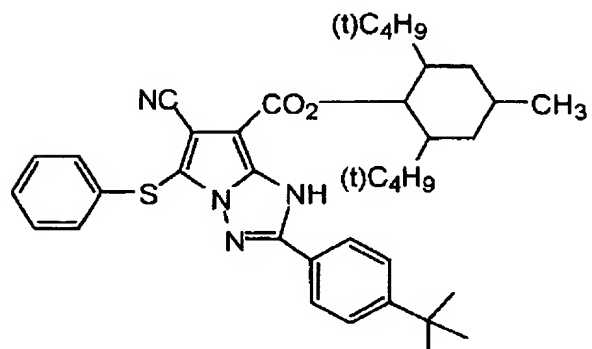
(69)



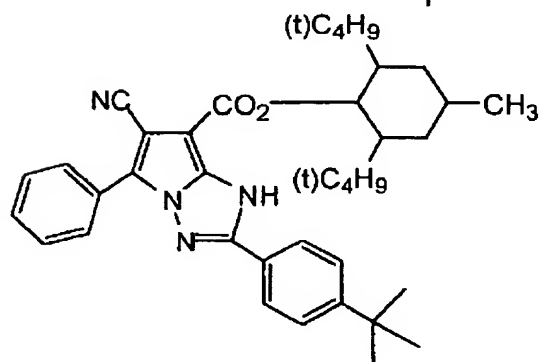
(70)



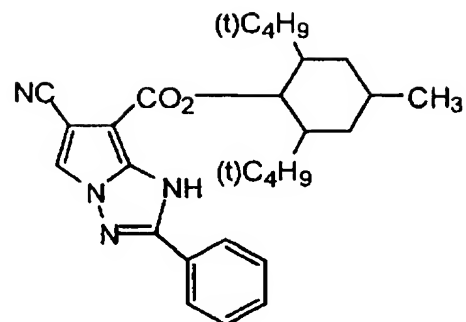
(71)



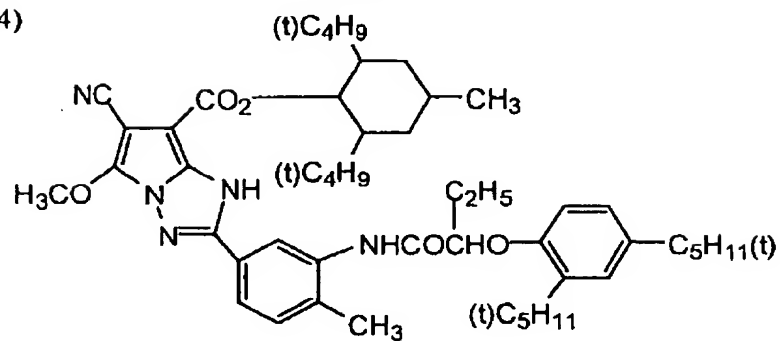
(72)



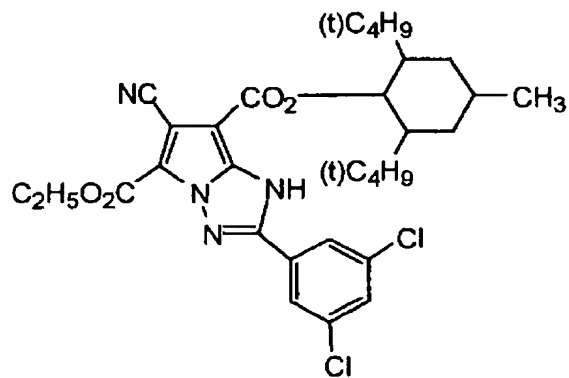
(73)



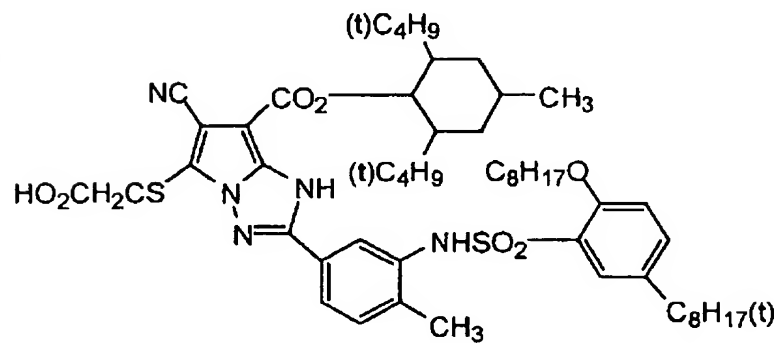
(74)



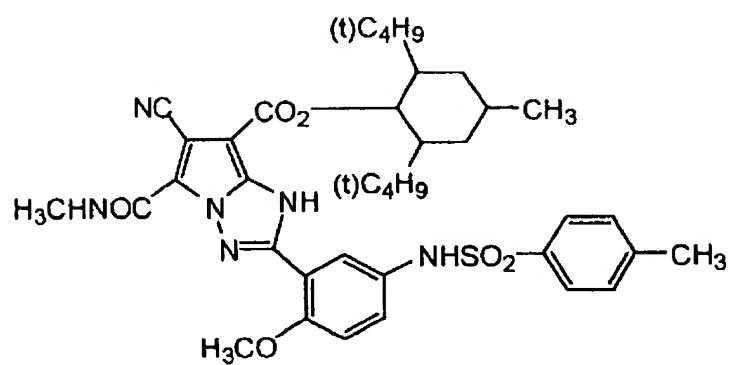
(75)



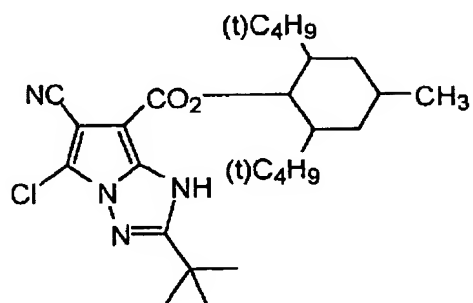
(76)



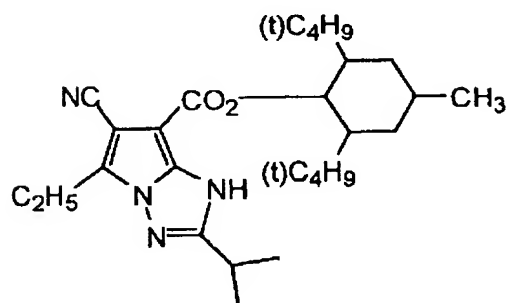
(77)



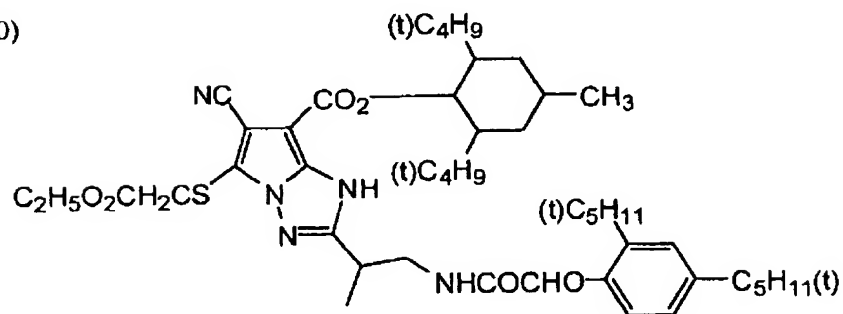
(78)



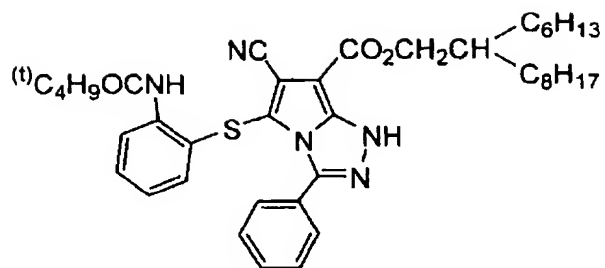
(79)



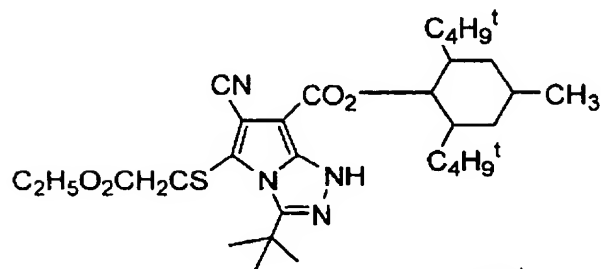
(80)



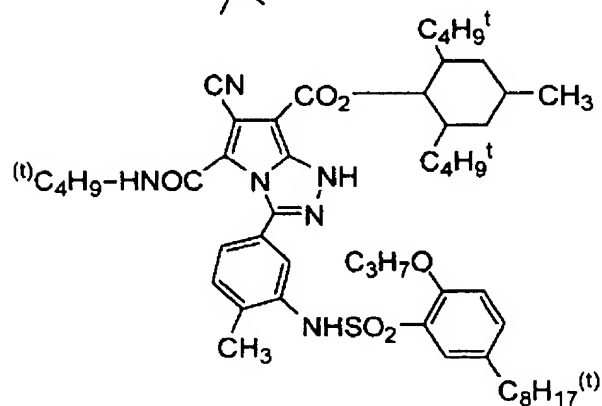
(81)



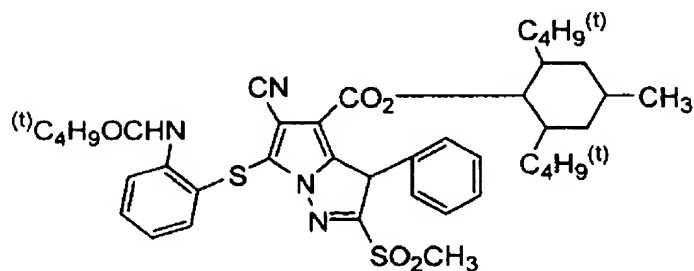
(82)



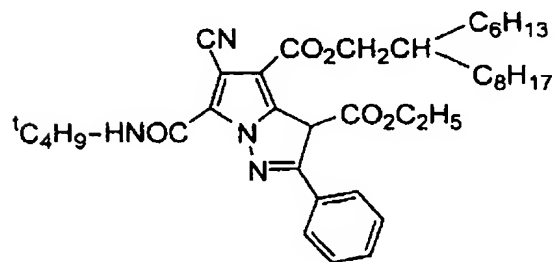
(83)



(84)



(85)



The compounds represented by the general formulae (A) and (B) according to the present invention

can be easily synthesized by the synthetic methods described in, for example, JP-A's-61-65245, 61-65246, 61-147254 and 8-122984.

5 The color photographic lightsensitive material of the present invention comprises a support and, superimposed thereon, at least one blue-sensitive silver halide emulsion layer, green-sensitive silver halide emulsion layer, red-sensitive silver halide emulsion layer and protective layer. It is preferred  
10 that each color-sensitive layer unit be composed of two or more layers of different speeds.

Further, it is preferred that the color photographic lightsensitive material be provided with not only the lightsensitive emulsion layers and  
15 protective layer but also various nonsensitive layers, such as a color mixing prevention layer, a yellow filter layer (simultaneously functioning as a color mixing prevention layer) and an antihalation layer.

Although the order of layer arrangement is not particularly limited, as a typical example, there can  
20 be mentioned a color photographic lightsensitive material comprising, arranged in the following sequence from the position most remote from a support toward the support, a protective layer, two or more blue-sensitive  
25 emulsion layers, a yellow filter layer (simultaneously functioning as a color mixing prevention layer), two or more green-sensitive emulsion layers, a color mixing

prevention layer, two or more red-sensitive emulsion layers, a color mixing prevention layer and an antihalation layer.

5       When each color-sensitive layer unit is composed of emulsion layers of different speeds, although the order of layer arrangement is not particularly limited, it is common practice to dispose an emulsion layer of higher speed at a position remoter from the support.

10       With respect to the blue-sensitive silver halide emulsion layer unit according to the present invention, when it means a unit composed of two or more blue-sensitive layers of different speeds, it is not necessary to dispose the two or more blue-sensitive layers adjacent to each other.

15       The green-sensitive silver halide emulsion layer unit and red-sensitive silver halide emulsion layer unit are the same as the above blue-sensitive silver halide emulsion layer unit except that the emulsion layers are sensitive to green and red, respectively.

20       For the purpose of sensitivity enhancement, as different from the above typical arrangement, the layer of highest speed of each of the units of different color sensitivities, namely, blue-, green- and red-sensitive emulsion layer units can be arranged on  
25       positions most remote from the support. That is, for example, there can be employed a layer arrangement comprising, disposed in the following sequence from the

position most remote from a support toward the support,  
a protective layer, a blue-sensitive emulsion layer of  
highest speed, a color mixing prevention layer, a  
green-sensitive emulsion layer of highest speed, a  
5 color mixing prevention layer, a red-sensitive emulsion  
layer of highest speed, a color mixing prevention  
layer, two or more blue-sensitive emulsion layers, a  
yellow filter layer (simultaneously functioning as a  
color mixing prevention layer), two or more green-  
10 sensitive emulsion layers, a color mixing prevention  
layer, two or more red-sensitive emulsion layers, a  
color mixing prevention layer and an antihalation  
layer.

Further, for the purpose of sensitivity  
15 enhancement, the layer arrangement can be such that a  
highest-speed layer unit consisting of a blue-sensitive  
emulsion layer of highest speed (if necessary, a color  
mixing prevention layer), a green-sensitive emulsion  
layer of highest speed (if necessary, a color mixing  
20 prevention layer) and a red-sensitive emulsion layer of  
highest speed (if necessary, a color mixing prevention  
layer) is disposed as an emulsion layer most remote  
from the support while furthermore, one or two or more  
blue-sensitive emulsion layers, a color mixing  
25 prevention layer, one or two or more green-sensitive  
emulsion layers, a color mixing prevention layer, one  
or two or more red-sensitive emulsion layers, a color



mixing prevention layer and an antihalation layer are disposed in this sequence toward the support.

5 Still further, for the purpose of sensitivity enhancement, the silver halide color photographic lightsensitive material can be appropriately provided with a light reflection layer so as to efficiently utilize light incident on the lightsensitive material. As the reflection substance contained in the light reflection layer, there can be mentioned any of  
10 micro-sized silver halide grains and inorganic crystals, such as those of  $\text{TiO}_2$ . For example, when micro-sized silver halide grains are used, it is preferred to set the grain thickness in conformity with given light wavelength for the purpose of attaining selective  
15 reflection of incident light wavelength.

The total amount of silver contained in the color photographic lightsensitive material of the present invention is preferably in the range of 3.0 to 8.5 g/m<sup>2</sup> in terms of coating amount.

20 The specific photographic speed of the color photographic lightsensitive material of the present invention, although not particularly limited, is preferably 640 or higher, more preferably 800 or higher. The use with a specific photographic speed of  
25 1000 or higher is most preferred from the viewpoint of exertion of the effect of the present invention.

The silver halide grains of the present invention

will be described at length below.

With respect to the halogen composition of the tabular grains of the present invention, the tabular grains are composed of silver halides containing silver iodide, namely, silver iodobromide or silver chloriodobromide.

In the present invention, a tabular grain is a silver halide grain having two opposing, parallel (111) main planes. A tabular grain of the present invention has one twin plane or two or more parallel twin planes. The twin plane is a (111) plane on the two sides of which ions at all lattice points have a mirror image relationship. When this tabular grain is viewed in a direction perpendicular to the main planes of the grain, it has any of triangular, square, hexagonal, and intermediate truncated triangular shapes, each having parallel outer surfaces.

The silver halide grains not comprehended in the tabular grains include regular crystal grains and grains having two or more nonparallel twin planes. The grains having two nonparallel twin planes include those having the configuration of a triangular pyramid or a rod. These are collectively referred to as "nontabular grains".

In the measurement of the equivalent circle diameter and thickness of the tabular grains, a transmission electron micrograph according to the

replica method is taken, from which the diameter of a circle having an area equal to the projected area of the parallel external surfaces of each individual grain (equivalent circle diameter) and the thickness thereof are determined. The grain thickness is calculated from the length of the shadow of the replica. With respect to the nontabular grains, the equivalent circle diameter is defined as the diameter of a circle having an area equal to the maximized projected area of each individual grain. When there is no plane parallel to a base as encountered in, for example, grains having the shape of a triangular pyramid among the nontabular grains, the thickness of the nontabular grains is defined as the distance between the base and the vortex thereof.

The nontabular grains are not favorable because the specific surface area thereof is so small that using them at a high proportion would cause a sensitivity enhancement to be difficult. A decrease of the equivalent circle diameter of tabular grains means a reduction of grain size and would render the attainment of sensitivity enhancement difficult. On the other hand, an increase of grain thickness means a decrease of specific surface area and would render the sustaining of high sensitivity/graininess ratio difficult.

In the silver halide photographic emulsion of the

present invention, 50% or more of all the silver halide grains are occupied by tabular grains of 1.0  $\mu\text{m}$  or greater equivalent circle diameter and 0.15  $\mu\text{m}$  or less grain thickness. In the silver halide photographic emulsions of the present invention, 50% or more of all the silver halide grains are preferably occupied by tabular grains of 1.5  $\mu\text{m}$  or greater equivalent circle diameter and 0.15  $\mu\text{m}$  or less grain thickness, and more preferably occupied by tabular grains of 2.0  $\mu\text{m}$  or greater equivalent circle diameter and 0.15  $\mu\text{m}$  or less grain thickness. Further, preferably, the equivalent circle diameter is not greater than 10  $\mu\text{m}$ , and the grain thickness is not less than 0.02  $\mu\text{m}$ .

The silver halide emulsion of the present invention is comprised of a photosensitive silver halide emulsion wherein 50% or more of all the silver halide grains are occupied by silver halide tabular grains having the above-mentioned composition and preferred configuration and having (111) faces as the main planes, the tabular grains composed of core portions of silver iodobromide which are free of growth ring structure and have a thickness of 0.1  $\mu\text{m}$  or less and shell portions having 10 or more dislocation lines at fringe areas thereof (the silver halide tabular grains hereinafter referred to as "tabular grains of the present invention").

In the tabular grains of the present invention,

the silver iodide content of core portions is preferably in the range of 1 to 40 mol%, more preferably 1 to 20 mol%, and most preferably 1 to 10 mol%.

5           The tabular grains of the present invention are characterized in that any growth ring structure is not observed in the core portions. The growth ring structure refers to a growth ring pattern observed when tabular grains are produced by carrying out growth of  
10 silver iodobromide according to the common DJ (main plane jet) method. It is considered as a transition of twinned crystal introduced by the presence of iodide ions, and considered as providing unwanted electron traps on grain surfaces. The growth ring structure is  
15 observed as lines parallel to grain sides. The growth ring structure can be observed in the same manner as employed in the observation of dislocation lines described later.

          As for the thin tabular grains like the tabular  
20 grains of the present invention, because of the large surface area, the above transition of twinned crystal has caused serious inefficiency.

          The tabular grains free of the above growth ring structure can be obtained by carrying out the grain  
25 growth according to the fine grain addition growth method in place of the common DJ method. With respect to this fine grain addition growth method, reference

can be made to, for example, JP-A-10-43570.

5       The tabular grains of the present invention have a grain thickness of 0.15  $\mu\text{m}$  or less and have 10 or more dislocation lines. The inventors have found that reducing of the thickness of core portions is preferred for enhancing the sensitivity of these grains. Reducing of the thickness of core portions, providing that the grain thickness is constant, leads to increase of the shell thickness. Since the occurrence of

10       dislocation lines is high in shell portions, an increase of the shell portion thickness would increase the occurrence of long dislocation lines. Although increasing of the number of dislocation lines is difficult in thin grains, this disadvantage would be

15       compensated for by increasing the length of dislocation lines. The thickness of the core portions of the tabular grains of the present invention is 0.1  $\mu\text{m}$  or less, preferably 0.09  $\mu\text{m}$  or less, and more preferably 0.08  $\mu\text{m}$  or less.

20       The core portions and the shell portions can be distinguished from each other by observing an extremely thin cross section of tabular grains, the cross section perpendicular to the main planes of the tabular grains, through a transmission electron microscope, and hence

25       the core portion thickness can be measured. The extremely thin cross section can be obtained by first applying a silver halide photographic emulsion onto a

support so as to produce a specimen comprising tabular grains arranged on the support in substantially parallel relationship to the support and thereafter cutting the specimen to a thickness of about 0.06  $\mu\text{m}$  by means of a diamond knife.

When an extremely thin section of tabular grains having dislocation lines introduced in the fringe portions is observed through a transmission electron microscope, generally four contrast straight lines parallel to the main planes are observed. These are classified into two lines close to the grain surface and two inner lines.

The two inner lines are attributed to twin planes. Most of the tabular grains contain two twin planes, so that the two lines corresponding thereto are observed. In such rare cases that there are three twin planes, three lines corresponding thereto are observed. In these cases, five lines are observed on the extremely thin section of tabular grains.

The two lines close to the main planes are attributed to the step of epitaxial growth of silver halide on fringe portions at the time of dislocation introduction. The silver halides for use in the epitaxial growth have a silver iodide content higher than that of the core grains and are grown under such conditions that deposition occurs mainly on the fringe portions. Under such conditions as well, however, a

small amount of phase with high silver iodide content is also formed on the main plane portions. This phase with high silver iodide content, because of the halogen composition difference from that of the surrounding portions, is observed as straight lines. That is, on the basis of these two lines as a border, the grain inner portions and the grain surface-side portions can be identified as the core portions and the shell portions, respectively.

10           In the present invention, tabular grains have dislocation lines. Dislocation lines in tabular grains can be observed by a direct method performed using a transmission electron microscope at a low temperature, as described in, e.g., J.F. Hamilton, Phot. Sci. Eng., 11, 57, (1967) or T. Shiozawa, J. Soc. Phot. Sci. Japan, 3, 5, 213, (1972). That is, silver halide grains, carefully extracted from an emulsion so as not to apply any pressure by which dislocations are produced in the grains, are placed on a mesh for electron microscopic observation. Observation is performed by a transmission method while the sample is cooled to prevent damage (e.g., print out) due to electron rays. In this observation, as the thickness of a grain is increased, it becomes more difficult to transmit electron rays through it. Therefore, grains can be observed more clearly by using an electron microscope of a high voltage type (200 kV or more for a



grain having a thickness of 0.25  $\mu\text{m}$ ). From photographs of grains obtained by the above method, it is possible to obtain the positions and the number of dislocations in each grain viewed in a direction perpendicular to the principal planes of the grain.

50% or more in number of all the silver halide grains contained in the silver halide emulsion of the present invention are occupied by tabular grains having dislocation lines of 10 or more, preferably 20 or more, and most preferably 30 or more. If dislocation lines are densely present or cross each other, it is sometimes impossible to correctly count dislocation lines per grain. Even in these situations, however, dislocation lines can be roughly counted to such an extent that their number is approximately 10, 20, or 30. This makes it possible to distinguish these grains from those in which obviously only a few dislocation lines are present. The average number of dislocation lines per grain is obtained as a number average by counting dislocation lines of 100 or more grains. Several hundreds of dislocation lines are sometimes found.

Dislocation lines can be introduced in, for example, the vicinity of the periphery of tabular grains. In this instance, the dislocation lines are nearly perpendicular to the periphery, and each dislocation line extends from a position corresponding

to x% of the distance from the center of tabular grains to the side (periphery) to the periphery. The value of x preferably ranges from 10 to less than 100, more preferably from 30 to less than 99, and most preferably from 50 to less than 98. In this instance, the figure created by binding the positions from which the dislocation lines start is nearly similar to the configuration of the grain. The created figure may be one which is not a complete similar figure but deviated. The dislocation lines of this type are not observed around the center of the grains. The dislocation lines are crystallographically oriented approximately in the (211) direction. However, the dislocation lines often meander and may also cross each other.

Dislocation lines may be positioned either nearly uniformly over the entire zone of the periphery of the tabular grains or on local points of the periphery. That is, referring to, for example, hexagonal tabular silver halide grains, dislocation lines may be localized either only in the vicinity of six vertexes or only in the vicinity of one of the vertexes. Contrarily, dislocation lines may be localized only in the sides excluding the vicinity of six vertexes.

Furthermore, dislocation lines may be formed over regions including the centers of two mutually parallel main planes of tabular grains. In the case where

dislocation lines are formed over the entire regions of the main planes, the dislocation lines may crystallographically be oriented approximately in the (211) direction when viewed in the direction perpendicular to the main planes, but the formation of the dislocation lines may be effected either in the (110) direction or randomly. Further, the length of each of the dislocation lines may be random, and the dislocation lines may be observed as short lines on the main planes or as long lines extending to the side (periphery). The dislocation lines may be straight or often meander. In many instances, the dislocation lines cross each other.

The position of dislocation lines may be limited to the periphery, main planes or local points as mentioned above, or the formation of dislocation lines may be effected on a combination thereof. That is, dislocation lines may be concurrently present on both the periphery and the main planes.

The introduction of dislocation lines in the tabular grains can be accomplished by disposing a specified phase of high silver iodide content within the grains. In the dislocation line introduction, the phase of high silver iodide content may be provided with discontinuous regions of high silver iodide content. Practically, the phase of high silver iodide content within the grains can be obtained by first

preparing base grains (core portions), then providing them with a phase of high silver iodide content and thereafter covering the outside thereof with a phase of silver iodide content lower than that of the phase of high silver iodide content. The silver iodide content of tabular grains as core portions is lower than that of the phase of high silver iodide content, and is preferably 0 to 20 mol%, more preferably 0 to 15 mol%.

The terminology "phase of high silver iodide content within the grains" refers to a silver halide solid solution containing silver iodide. The silver halide of this solid solution is preferably silver iodide, silver iodobromide or silver chloriodobromide, more preferably silver iodide or silver iodobromide (the silver iodide content is in the range of 10 to 40 mol% based on the silver halides contained in the phase of high silver iodide content). For selectively causing the phase of high silver iodide content within the grains (hereinafter referred to as "internal high silver iodide phase") to be present on any of the sides, corners and planes of the base grains, it is desirable to control forming conditions for the base grains, forming conditions for the internal high silver iodide phase and forming conditions for the phase covering the outside thereof.

Important factors as the formation conditions of a substrate grain are the  $pAg$  (the logarithm of the

reciprocal of a silver ion concentration), the presence/absence, type, and amount of a silver halide solvent, and the temperature. By controlling the pAg to preferably 8.5 or less, more preferably, 8 or less  
5 during the growth of substrate grains, the internal silver iodide rich phase can be made to selectively exist in portions near the corners or on the surface of the substrate grain, when this silver iodide rich phase is formed later.

10 On the other hand, by controlling the pAg to preferably 8.5 or more, more preferably, 9 or more during the growth of substrate grains, the internal silver iodide rich phase can be made to exist on the edges of the substrate grain.

15 The threshold value of the pAg rises and falls depending on the temperature and the presence/absence, type, and amount of a silver halide solvent. When thiocyanate is used as the silver halide solvent, this threshold value of the pAg shifts to higher values.

20 The value of the pAg at the end of the growth of substrate grains is particularly important, among other pAg values during the growth. On the other hand, even if the pAg during the growth does not meet the above value, the position of the internal silver iodide rich  
25 phase can be controlled by performing ripening by controlling the pAg to the above proper value after the growth of substrate grains. In this case, ammonia, an

amine compound, a thiourea derivative, or thiocyanate salt can be effectively used as the silver halide solvent. The internal silver iodide rich phase can be formed by a so-called conversion method.

5           This method includes a method which, at a certain point during grain formation, adds halogen ion smaller in solubility for salt for forming silver ion than halogen ion that forms grains or portions near the surfaces of grains at that point. In the present  
10           invention, the amount of halogen ion having a smaller solubility to be added preferably takes a certain value (related to a halogen composition) with respect to the surface area of grains at that point. For example, at a given point during grain formation, it is preferable  
15           to add a certain amount or more of KI with respect to the surface area of silver halide grains at that point. More specifically, it is preferable to add  $8.2 \times 10^{-5}$  mol/m<sup>2</sup> or more of iodide salt.

          A more preferable method of forming the internal  
20           silver iodide rich phase is to add an aqueous silver salt solution simultaneously with addition of an aqueous silver halide solution containing iodide salt.

          As an example, an aqueous AgNO<sub>3</sub> solution is added simultaneously with addition of an aqueous KI solution  
25           by the main plane-jet method. In this case, the addition start timings and the addition end timings of the aqueous KI solution and the aqueous AgNO<sub>3</sub> solution

can be shifted from each other. The addition molar ratio of the aqueous  $\text{AgNO}_3$  solution to the aqueous KI solution is preferably 0.1 or more, more preferably, 0.5 or more, and most preferably, 1 or more. The total addition molar quantity of the aqueous  $\text{AgNO}_3$  solution can exit in a silver excess region with respect to halogen ion in the system and iodine ion added. During the addition of the aqueous silver halide solution containing iodine ion and the addition of the aqueous silver salt solution by the main plane-jet method, the pAg preferably decreases with the addition time by the main plane-jet. The pAg before the addition is preferably 6.5 to 13, and more preferably, 7.0 to 11. The pAg at the end of the addition is most preferably 6.5 to 10.0.

In carrying out the above method, the solubility of a silver halide in the mixing system is preferably as low as possible. Therefore, the temperature of the mixing system at which the silver iodide rich phase is formed is preferably 30°C to 80°C, and more preferably, 30°C to 70°C.

The formation of the internal silver iodide rich phase is most preferably performed by adding fine-grain silver iodide, fine-grain silver iodobromide, fine-grain silver chloriodide, or fine-grain silver bromochloriodide. The addition of fine-grain silver iodide is particularly preferred. These fine grains

normally have a grain size of 0.01 to 0.1  $\mu\text{m}$ , but those having a grain size of 0.01  $\mu\text{m}$  or less or 0.1  $\mu\text{m}$  or more can also be used. Methods of preparing these fine silver halide grains are described in JP-A's-1-183417, 2-44335, 1-183644, 1-183645, 2-43534, and 2-43535, the disclosures of which are incorporated herein by reference. The internal silver iodide rich phase can be formed by adding and ripening these fine silver halide grains. In dissolving the fine grains by ripening, the silver halide solvent described above can also be used. These fine grains added need not immediately, completely dissolve to disappear but need only disappear by dissolution when the final grains are completed.

The internal silver iodide rich phase is located in a region of, when measuring from the center of, e.g., a hexagon formed in a plane by projecting a grain thereon, preferably 5 to less than 100 mol%, more preferably, 20 to less than 95 mol%, and most preferably, 50 to less than 90 mol% with respect to the total silver amount of the grain. The amount of a silver halide which forms the internal silver iodide rich phase is, as a silver amount, preferably 50 mol% or less, and more preferably, 20 mol% or less of the total silver amount of a grain. These values of amounts of the silver iodide rich phase are not those obtained by measuring the halogen composition of the



final grain by using various analytical methods but formulated values in the producing of a silver halide emulsion. The internal silver iodide rich phase often disappears from the final grain owing to, e.g.,

5 recrystallization, and so all silver amounts described above are related to their formulated values.

It is, therefore, readily possible to observe dislocation lines in the final grains by the above method, but the internal silver iodide rich phase  
10 introduced to introduce dislocation lines cannot be observed as a definite phase in many cases because the silver iodide composition in the boundary continuously changes. The halogen compositions in each portion of a grain can be checked by combining X-ray diffraction, an  
15 EPMA (also called an XMA) method (a method of scanning a silver halide grain by electron rays to detect its silver halide composition), and an ESCA (also called an XPS) method (a method of radiating X-rays to spectroscopically detect photoelectrons emitted from  
20 the surface of a grain).

The silver iodide content of an outer phase covering the internal silver iodide rich phase is lower than that of the silver iodide rich phase, and is preferably 0 to 30 mol%, more preferably, 0 to 20 mol%,  
25 and most preferably, 0 to 10 mol% with respect to a silver halide amount contained in the outer phase.

Although the temperature and the pAg, at which the

outer phase covering the internal silver iodide rich phase is formed, can take arbitrary values, the temperature is preferably 30°C to 80°C, and most preferably, 35°C to 70°C, and the pAg is preferably 6.5 to 11.5. The use of the silver halide solvents described above is sometimes preferable, and the most preferable silver halide solvent is thiocyanate salt.

Another method of introducing dislocation lines to tabular grains is to use an iodide ion releasing agent as described in JP-A-6-11782, the disclosure of which is incorporated herein by reference. This method is also preferably used.

Dislocation lines can also be introduced by appropriately combining this dislocation line introducing method with the above-mentioned dislocation line introducing method.

In the chemical sensitization of silver halide grains, nonuniformity between grains in, for example, the size thereof would cause attaining the optimum sensitization of the individual grains to be difficult, thereby inviting a deterioration of photographic sensitivity. From this viewpoint, it is preferred that the equivalent circle diameter and thickness of silver halide tabular grains according to the present invention be monodisperse. With respect to all the silver halide grains of the present invention, the variation coefficient of equivalent circle diameter is

preferably 40% or less, more preferably 30% or less,  
and even more preferably 20% or less. With respect to  
all the silver halide grains, the variation coefficient  
of thickness is preferably 20% or less. The  
5 terminology "variation coefficient of equivalent circle  
diameter" used herein means the value obtained by  
dividing a standard deviation of equivalent circle  
diameters of individual silver halide grains by an  
average equivalent circle diameter and by multiplying  
10 the quotient by 100. On the other hand, the  
terminology "variation coefficient of thickness" used  
herein means the value obtained by dividing a standard  
deviation of thicknesses of individual silver halide  
grains by an average thickness and by multiplying the  
15 quotient by 100.

The twin plane spacing of the tabular grains is  
preferably 0.014  $\mu\text{m}$  or less, more preferably 0.012  $\mu\text{m}$   
or less. In the formation of fringe dislocation type  
grains, uniformity of the side faces of tabular grains  
20 is important because it influences the uniformity of  
fringe dislocation between individual grains. From  
this viewpoint, with respect to the twin plane spacing,  
it is preferred that the variation coefficient of twin  
plane spacing of tabular grains be 40% or less,  
25 especially 30% or less. The terminology "fringe  
dislocation type grains" used herein means grains  
having dislocation lines at fringe portions thereof

upon viewing the tabular grains from the main plane side thereof.

5       The tabular grains having (111) faces as main planes generally have the shape of a hexagon, a triangle or an intermediate triangle with angle portions cut off, and have three-fold symmetry. With respect to the six sides, the ratio of the length of three relatively long sides to that of three relatively short sides is referred to as the ratio of long  
10       side/short side. The triangle with angle portions cut off refers to the shape resulting from cutting off of angle portions of a triangle. In the formation of fringe dislocation type grains, it has been observed that the density of dislocation lines at the fringe  
15       portions is lower in the grains having the shape close to a triangle than in the grains having the shape close to a hexagon. It is preferred that the ratio of long side/short side of tabular grains be close to 1. The average of the ratio of long side/short side of tabular  
20       grains is preferably 1.6 or less, more preferably 1.3 or less.

      The tabular grains for use in the present invention are formed through the steps of nucleation, Ostwald ripening and growth. Although all of these  
25       steps are important for suppressing the spread of grain size distribution, attention should be paid so as to prevent the spread of size distribution at the first

nucleation step because it is difficult to narrow the spread of size distribution brought about in a previous step by an ensuing step. What is important in the nucleation step is the relationship between the

5 temperature of reaction mixture and the period of nucleation comprising adding silver ions and bromide ions to a reaction mixture according to the main plane jet technique and producing precipitates.

JP-A-63-92942 by Saito describes that it is preferred  
10 that the temperature of the reaction mixture at the time of nucleation be in the range of from 20 to 45°C for realizing a monodispersity enhancement. Further, JP-A-2-222940 by Zola et al describes that the suitable temperature at nucleation is 60°C or below.

15 Supplemental addition of gelatin may be effected during the grain formation in order to obtain thin grain thickness, monodisperse tabular grains. The added gelatin is preferably a chemically modified gelatin as described in JP-A's-10-148897 and 11-143002.

20 This chemically modified gelatin is a gelatin characterized in that at least two carboxyl groups have newly been introduced at a chemical modification of amino groups contained in the gelatin, and it is preferred that gelatin trimellitate be used as the  
25 same. Also, gelatin succinate is preferably used. The chemically modified gelatin is preferably added prior to the growth step, more preferably immediately after

the nucleation. The addition amount thereof is preferably 60% or greater, more preferably 80% or greater, and most preferably 90% or greater, based on the total mass of dispersion medium used in grain formation.

Although the composition of the tabular grain used in the present invention is not limited, it is preferably silver iodobromide or silver chloriodobromide.

The silver chloride content is preferably 8 mol% or less, more preferably 3 mol% or less, and most preferably 0 mol%. With respect to the silver iodide content, it is preferably 20 mol% or less inasmuch as the variation coefficient of the grain size distribution of the tabular grain emulsion is preferably 30% or less. The lowering of the variation coefficient of the distribution of equivalent circle diameter of the tabular grain emulsion can be facilitated by decreasing the silver iodide content.

It is especially preferred that the variation coefficient of the grain size distribution of the tabular grain emulsion be 20% or less while the silver iodide content be 10 mol% or less.

Furthermore, it is preferred that the tabular grains have some intragranular structure with respect to the silver iodide distribution. The silver iodide distribution may have a main plane structure, a treble

structure, a quadruple structure or a structure of higher order.

The variation coefficient of the inter-grain silver iodide content distribution of silver halide grains used in the present invention is preferably 20% or less, more preferably, 15% or less, and most preferably, 10% or less. If the variation coefficient of the silver iodide content is larger than 20%, no high contrast can be obtained in the photographic properties, and a reduction of the sensitivity upon application of a pressure increases.

Any known method can be used as a method of producing silver halide grains having a narrow inter-grain silver iodide content distribution. Examples are a method of adding fine grains as disclosed in JP-A-1-183417 and a method which uses an iodide ion releasing agent as disclosed in JP-A-2-68538, the disclosures of which are incorporated herein by reference. These methods can be used alone or in combination.

The silver iodide content of each grain can be measured by analyzing the composition of the grain by using an X-ray microanalyzer. The variation coefficient of an inter-grain silver iodide content distribution is a value defined by

$$\frac{(\text{standard deviation} / \text{average silver iodide content}) \times 100}{100} = \text{variation coefficient (\%)}$$

by using the standard deviation of silver iodide contents and the average silver iodide content when the silver iodide contents of at least 100, more preferably, 200, and most preferably, 300 emulsion grains are measured. The measurement of the silver iodide content of each individual grain is described in, e.g., European Patent 147,868. A silver iodide content  $Y_i$  [mol%] and an equivalent-sphere diameter  $X_i$  [ $\mu\text{m}$ ] of each grain sometimes have a correlation and sometimes do not. However,  $Y_i$  and  $X_i$  desirably have no correlation. The halogen composition structure of a tabular grain of the present invention can be checked by combining, e.g., X-ray diffraction, an EPMA (also called an XMA) method (a method of scanning a silver halide grain by electron rays to detect its silver halide composition), and an ESCA (also called an XPS) method (a method of radiating X-rays to spectroscopically detect photoelectrons emitted from the surface of a grain). When the silver iodide content is measured in the present invention, the grain surface is a region about 5 nm deep from the surface, and the grain interior is a region except for the surface. The halogen composition of this grain surface can usually be measured by the ESCA method.

Silver halide emulsions of the present invention can also be subjected to reduction sensitization during grain formation, after grain formation and before or



during chemical sensitization, or after chemical sensitization.

Reduction sensitization can be selected from a method of adding reduction sensitizers to a silver halide emulsion, a method called silver ripening in which grains are grown or ripened in a low-pAg ambient at pAg 1 to 7, and a method called high-pH ripening in which grains are grown or ripened in a high-pH ambient at pH 8 to 11. Two or more of these methods can also be used together.

The method of adding reduction sensitizers is preferred in that the level of reduction sensitization can be finely adjusted.

Known examples of reduction sensitizers are stannous salt, ascorbic acid and its derivative, amines and polyamines, a hydrazine derivative, formamidinesulfinic acid, a silane compound, and a borane compound. In reduction sensitization of the present invention, it is possible to selectively use these known reduction sensitizers or to use two or more types of compounds together. Preferred compounds as reduction sensitizers are stannous chloride, thiourea dioxide, dimethylamineborane, and ascorbic acid and its derivative. Although the addition amount of reduction sensitizers must be so selected as to meet the emulsion producing conditions, a preferable amount is  $10^{-7}$  to  $10^{-3}$  mol per mol of a silver halide.

Reduction sensitizers are dissolved in water or an organic solvent such as alcohols, glycols, ketones, esters, or amides, and the resultant solution is added during grain growth. Although adding to a reactor vessel in advance is also preferred, adding at a given timing during grain growth is more preferred. It is also possible to add reduction sensitizers to an aqueous solution of a water-soluble silver salt or of a water-soluble alkali halide to precipitate silver halide grains by using this aqueous solution. Alternatively, a solution of reduction sensitizers can be added separately several times or continuously over a long time period with grain growth.

It is preferable to use an oxidizer for silver during the process of producing emulsions of the present invention. An oxidizer for silver is a compound having an effect of converting metal silver into silver ion. A particularly effective compound is the one that converts very fine silver grains, formed as a by-product in the process of formation and chemical sensitization of silver halide grains, into silver ion. The silver ion produced can form a silver salt hard to dissolve in water, such as a silver halide, silver sulfide, or silver selenide, or a silver salt easy to dissolve in water, such as silver nitrate. An oxidizer for silver can be either an inorganic or organic substance. Examples of an inorganic oxidizer

are ozone, hydrogen peroxide and its adduct (e.g.,  
NaBO<sub>2</sub>·H<sub>2</sub>O<sub>2</sub>·3H<sub>2</sub>O, 2NaCO<sub>3</sub>·3H<sub>2</sub>O<sub>2</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O<sub>2</sub>, and  
2Na<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O), peroxy acid salt (e.g., K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>,  
K<sub>2</sub>C<sub>2</sub>O<sub>6</sub>, and K<sub>2</sub>P<sub>2</sub>O<sub>8</sub>), a peroxy complex compound (e.g.,  
5 K<sub>2</sub>[Ti(O<sub>2</sub>)C<sub>2</sub>O<sub>4</sub>]·3H<sub>2</sub>O, 4K<sub>2</sub>SO<sub>4</sub>·Ti(O<sub>2</sub>)OH·SO<sub>4</sub>·2H<sub>2</sub>O, and  
Na<sub>3</sub>[VO(O<sub>2</sub>)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O]), permanganate (e.g., KMnO<sub>4</sub>),  
an oxyacid salt such as chromate (e.g., K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), a  
halogen element such as iodine and bromine,  
perhalogenate (e.g., potassium periodate), a salt of a  
10 high-valence metal (e.g., potassium  
hexacyanoferrate(II)), and thiosulfonate.

Examples of an organic oxidizer are quinones such  
as p-quinone, an organic peroxide such as peracetic  
acid and perbenzoic acid, and a compound for releasing  
15 active halogen (e.g., N-bromosuccinimide, chloramine T,  
and chloramine B).

Preferable oxidizers of the present invention are  
inorganic oxidizers such as ozone, hydrogen peroxide  
and its adduct, a halogen element, and thiosulfonate,  
20 and organic oxidizers such as quinones.

It is preferable to use the reduction  
sensitization described above and the oxidizer for  
silver together. In this case, the reduction  
sensitization can be performed after the oxidizer is  
25 used or vice versa, or the oxidizer can be used  
simultaneously with the reduction sensitization. These  
methods can be applied to both the grain formation step

and the chemical sensitization step.

Metal complexes can be added to the silver halide emulsion of the present invention during grain formation, after grain formation and before or during chemical sensitization. Also, metal complexes can be  
5 divisionally added a plurality of times. However, 50% or more of the total content of metal complexes contained in a silver halide grain are preferably contained in a layer 1/2 or less as a silver amount  
10 from the outermost surface of the grain. A layer not containing metal complexes can also be formed on the outside, i.e., on the side away from a support, of the layer containing metal complexes herein mentioned.

These metal complexes are preferably contained by  
15 dissolving them in water or an appropriate solvent and directly adding the solution to a reaction solution during the formation of silver halide grains, or by forming silver halide grains by adding them to an aqueous silver salt solution, aqueous silver salt  
20 solution, or some other solution for forming the grains. Alternatively, these metal complexes are also favorably contained by adding and dissolving fine silver halide grains previously made to contain the metal complexes, and depositing these grains on other  
25 silver halide grains.

When these metal complexes are to be added, the hydrogen ion concentration in a reaction solution is

such that the pH is preferably 1 to 10, and more preferably, 3 to 7.

Silver halide emulsions of the present invention are preferably subjected to selenium sensitization.

5       As selenium sensitizers usable in the present invention, selenium compounds disclosed in conventionally known patents can be used. Usually, a labile selenium compound and/or a non-labile selenium compound is used by adding it to an emulsion and stirring the  
10       emulsion at a high temperature, preferably 40°C or more for a predetermined period of time. As non-labile selenium compounds, it is preferable to use compounds described in, e.g., Jpn. Pat. Appln. KOKOKU Publication No. (hereinafter referred to as JP-B-)44-15748,  
15       JP-B-43-13489, and JP-A's-4-25832 and 4-109240, the disclosures of which are incorporated herein by reference.

      The non-labile selenium sensitizer refers to the sensitizer which causes the amount of silver selenide  
20       formed upon the addition of non-labile selenium sensitizer only without the use of any nucleophilic agent to be 30% or less based on the amount of added non-labile selenium sensitizer. As the non-labile selenium sensitizer, there can be mentioned compounds  
25       described in, for example, JP-B's-46-4553, 52-34492 and 52-34491. When the non-labile selenium sensitizer is used, it is preferred to simultaneously use a

nucleophilic agent. As the nucleophilic agent, there can be mentioned compounds described in, for example, JP-A-9-15776.

Selenium sensitization can be achieved more  
5 effectively in the presence of a silver halide solvent.

Examples of a silver halide solvent usable in the present invention are (a) organic thioethers described in, e.g., U.S.P.'s 3,271,157, 3,531,289, and 3,574,628, and JP-A's-54-1019 and 54-158917, the disclosures of  
10 which are incorporated herein by reference, (b) thiourea derivatives described in, e.g., JP-A's-53-82408, 55-77737, and 55-2982, the disclosures of which are incorporated herein by reference, (c) a silver halide solvent having a thiocarbonyl group  
15 sandwiched between an oxygen or sulfur atom and a nitrogen atom, described in, e.g., JP-A-53-144319, the disclosure of which is incorporated herein by reference, (d) imidazoles described in, e.g., JP-A-54-100717, the disclosure of which is incorporated  
20 herein by reference, (e) sulfite, and (f) thiocyanate.

Most preferred examples of a silver halide solvent are thiocyanate and tetramethylthiourea. Although the amount of a solvent to be used changes in accordance with its type, a preferred amount is, for example,  
25  $1 \times 10^{-4}$  to  $1 \times 10^{-2}$  mol per mol of a silver halide.

A gold sensitizer for use in gold sensitization of the present invention can be any compound having an

oxidation number of gold of +1 or +3, and it is possible to use gold compounds normally used as gold sensitizers. Representative examples are chloroaurate, potassium chloroaurate, aurictrichloride, potassium auricthiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyltrichloro gold, gold sulfide, and gold selenide. Although the addition amount of gold sensitizers changes in accordance with various conditions, the amount is preferably  $1 \times 10^{-7}$  to  $5 \times 10^{-5}$  mol per mol of a silver halide.

Emulsions of the present invention are preferably subjected to sulfur sensitization during chemical sensitization.

This sulfur sensitization is commonly performed by adding sulfur sensitizers and stirring the emulsion for a predetermined time at a high temperature, preferably 40°C or more.

Sulfur sensitizers known to those skilled in the art can be used in sulfur sensitization. Examples are thiosulfate, allylthiocarbamidothiourea, allylisothiocyanate, cystine, p-toluenethiosulfonate, and rhodanine. It is also possible to use sulfur sensitizers described in, e.g., U.S.P.'s 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, and 3,656,955, German Patent 1,422,869, JP-B-56-24937, and JP-A-55-45016, the disclosures of which are incorporated herein by reference. The addition amount

of sulfur sensitizers need only be large enough to effectively increase the sensitivity of an emulsion. This amount changes over a wide range in accordance with various conditions, such as the pH, the  
5 temperature, and the size of silver halide grains. However, the amount is preferably  $1 \times 10^{-7}$  to  $5 \times 10^{-5}$  mol per mol of a silver halide.

The photographic emulsion of the present invention is preferably subjected to a spectral sensitization  
10 with at least one methine dye or the like, from the viewpoint that the effects desired in the present invention can be exerted. Examples of usable dyes include cyanine dyes, merocyanine dyes, composite  
15 cyanine dyes, composite merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly useful dyes are those belonging to cyanine dyes, merocyanine dyes and composite merocyanine dyes. Any of nuclei commonly  
20 used in cyanine dyes as basic heterocyclic nuclei can be contained in these dyes. Examples of such applicable nuclei include a pyrroline nucleus, an oxazoline nucleus, a thiozoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole  
25 nucleus and a pyridine nucleus; nuclei comprising these nuclei fused with alicyclic hydrocarbon rings; and nuclei comprising these nuclei fused with aromatic



hydrocarbon rings, such as an indolenine nucleus, a  
benzindolenine nucleus, an indole nucleus, a  
benzoxazole nucleus, a naphthoxazole nucleus, a  
benzothiazole nucleus, a naphthothiazole nucleus, a  
5 benzoselenazole nucleus, a benzimidazole nucleus and a  
quinoline nucleus. These nuclei may have at least one  
substituent on carbon atoms thereof.

Any of 5 or 6-membered heterocyclic nuclei such as  
a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a  
10 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-  
dione nucleus, a rhodanine nucleus and a thiobarbituric  
acid nucleus can be applied as a nucleus having a  
ketomethylene structure to the merocyanine dye or  
composite merocyanine dye.

15 These spectral sensitizing dyes may be used  
either individually or in combination. The spectral  
sensitizing dyes are often used in combination for  
the purpose of attaining supersensitization.  
Representative examples thereof are described in  
20 U.S.P.'s 2,688,545, 2,977,229, 3,397,060, 3,522,052,  
3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898,  
3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862  
and 4,026,707, and GB 1,344,281 and 1,507,803,  
JP-B's-43-4936 and 53-12375 and JP-A's-52-110618 and  
25 52-109925.

The emulsion of the present invention may be doped  
with a dye which itself exerts no spectral sensitizing

effect or a substance which absorbs substantially none of visible radiation and exhibits supersensitization, together with the above spectral sensitizing dye.

5       The emulsion may be doped with the spectral sensitizing dye at any stage of the process for preparing the emulsion which is known as being useful. Although the doping is most usually conducted at a stage between the completion of the chemical sensitization and before the coating, the spectral  
10       sensitizing dye can be added simultaneously with the chemical sensitizer to thereby simultaneously effect the spectral sensitization and the chemical sensitization as described in U.S.P.'s. 3,628,969 and 4,225,666. Alternatively, the spectral sensitization  
15       can be conducted prior to the chemical sensitization as described in JP-A-58-113928, and also, the spectral sensitizing dye can be added prior to the completion of silver halide grain precipitation to thereby initiate the spectral sensitization. Further, the above  
20       compound can be divided prior to addition, that is, part of the compound can be added prior to the chemical sensitization with the rest of the compound added after the chemical sensitization as taught in U.S.P. 4,225,666. Still further, the spectral  
25       sensitizing dye can be added at any stage during the formation of silver halide grains, such as the method disclosed in U.S.P. 4,183,756 and other methods.

The addition amount of sensitizing dyes can be  $4 \times 10^{-6}$  to  $8 \times 10^{-3}$  mol per mol of a silver halide. For a silver halide grain size of average equivalent-sphere diameter 0.2 to 1.2  $\mu\text{m}$ , an addition amount of  
5 about  $5 \times 10^{-5}$  to  $2 \times 10^{-3}$  mol is more effective.

Fog occurring while a silver halide emulsion of the present invention is aged can be improved by adding and dissolving a previously prepared silver iodobromide emulsion during chemical sensitization. This silver  
10 iodobromide emulsion can be added at any timing during chemical sensitization. However, it is preferable to first add and dissolve the silver iodobromide emulsion and then add sensitizing dyes and chemical sensitizers in this order. The silver iodobromide emulsion used  
15 has an silver iodide content lower than the surface silver iodide content of a host grain, and is preferably a pure silver bromide emulsion. The size of this silver iodobromide emulsion is not limited as long as the emulsion can be completely dissolved. However,  
20 the equivalent-sphere diameter is preferably 0.1  $\mu\text{m}$  or less, and more preferably, 0.05  $\mu\text{m}$  or less. Although the addition amount of the silver iodobromide emulsion changes in accordance with a host grain used, the amount is basically preferably 0.005 to 5 mol%, and  
25 more preferably, 0.1 to 1 mol% per mol of silver.

In order to upgrade the color reproduction, a donor layer (CL) of interlayer effect having a spectral

sensitivity distribution different from those of main  
lightsensitive layers BL, GL and RL as described in  
U.S.P.'s 4,663,271, 4,705,744 and 4,707,436 and  
JP-A's-62-160448 and 63-89850 is preferably arranged  
5 adjacent to or close to the main lightsensitive layers.

The silver halide color photographic light-  
sensitive material of the present invention has a  
protective layer. The protective layer refers to a  
layer superimposed on a lightsensitive layer most  
10 remote from the support on a surface side of the  
lightsensitive layer. JP-A-5-34857 describes that the  
sharpness can be upgraded by reducing the thickness of  
the protective layer and that tabular grains can be  
preferably used because of the less degree of light  
15 scattering.

However, as a result of investigations, it has  
become apparent that when use is made of tabular grains  
whose thickness is as small as 0.15  $\mu\text{m}$  or less, the  
light scattering by the tabular grains rather tends to  
20 increase. Although it is considered that simultaneous  
use of the protective layer and the tabular grains is  
not favorable in such a case from the viewpoint of  
sharpness, it has been found that when use is made of  
the tabular grains of the present invention, high  
25 sensitivity can be attained with lowering of sharpness  
suppressed by combination thereof with a thin  
protective layer. In the silver halide color

photographic lightsensitive material of the present invention, the thickness of the protective layer is preferably 3  $\mu\text{m}$  or less, more preferably in the range of 2 to 0.5  $\mu\text{m}$ . When the protective layer consists of  
5 two or more layers, the thickness of protective layer refers to the sum of layer thicknesses.

The thickness of films including the protective layer is measured in the following manner. Specimen is conditioned in a relative humidity of 55% at 25°C for  
10 2 days, and the thickness thereof is measured by means of commercially available contact type film thickness meter (K-402 BSTAND manufactured by Anritsu Electric Co., Ltd.). The total thickness of all the hydrophilic colloid layers disposed on the emulsion layer side is  
15 calculated as a difference between the thickness of sample and that of sample from which the coating layers on the support have been removed. The thickness of each of the layers of a multilayer silver halide color lightsensitive material can be measured by taking a  
20 magnified photograph of a section thereof by means of a scanning electron microscope. In the measurement by means of a scanning electron microscope, the specimen must generally be measured in vacuum to thereby  
25 disenable maintaining the state of conditioned specimen, so that loss of water and substances of relatively low boiling point from the specimen may result in inaccurate thickness measuring. Therefore,

specimen forming methods, such as freeze dry, are being tested, but none of them is satisfactory. The measuring by photographing of a section with the use of a scanning electron microscope is utilized as measuring means for calculating the thickness of each layer of dry sample on the basis of the total film thickness measured with the use of a contact type film thickness meter.

In the present invention, a non-light-sensitive fine-grain silver halide is preferably used. The non-light-sensitive fine-grain silver halide preferably consists of silver halide grains which are not exposed during imagewise exposure for obtaining a dye image and are not substantially developed during development.

These silver halide grains are preferably not fogged in advance. In the non-light-sensitive fine-grain silver halide, the content of silver bromide is 0 to 100 mol%, and silver chloride and/or silver iodide can be added if necessary. The non-light-sensitive fine-grain silver halide preferably contains 0.5 to 10 mol% of silver iodide. The average grain size (the average value of equivalent-circle diameters of projected areas) of the fine-grain silver halide is preferably 0.01 to 0.5  $\mu\text{m}$ , and more preferably, 0.02 to 2  $\mu\text{m}$ .

The non-light-sensitive fine-grain silver halide can be prepared following the same procedures as for a common light-sensitive silver halide. The surface of

the non-light-sensitive fine-grain silver halide need not be optically sensitized nor spectrally sensitized. However, before the silver halide grains are added to a coating solution, it is preferable to add a well-known stabilizer such as a triazole-based compound, azaindene-based compound, benzothiazolium-based compound, mercapto-based compound, or zinc compound. Colloidal silver can be added to this fine-grain silver halide grain-containing layer.

The present invention can be applied to not only black-and-white printing paper, black-and-white negative film and X-ray film but also various color lightsensitive materials such as color negative film for general purposes or cinema, color reversal film for slide or TV, color paper, color positive film and color reversal paper. Moreover, the present invention is suitable to lens equipped film units described in JP-B-2-32615 and Jpn. Utility Model Appln. KOKOKU Publication No. 3-39784.

Supports which can be appropriately used in the present invention are described in, e.g., the aforementioned RD. No. 17643, page 28; RD. No. 18716, from the right column of page 647 to the left column of page 648; and RD. No. 307105, page 879.

In the lightsensitive material of the present invention, hydrophilic colloid layers (referred to as "back layers") having a total dry film thickness of 2

to 20  $\mu\text{m}$  are preferably provided on the side opposite to the side having emulsion layers. These back layers preferably contain the aforementioned light absorbent, filter dye, ultraviolet absorbent, antistatic agent, film hardener, binder, plasticizer, lubricant, coating aid and surfactant. The swelling ratio of these back layers is preferably in the range of 150 to 500%.

The lightsensitive material according to the present invention can be developed by conventional methods described in the aforementioned RD. No. 17643, pages 28 and 29; RD. No. 18716, page 651, left to right columns; and RD No. 307105, pages 880 and 881.

The color negative film processing solution for use in the present invention will be described below.

The compounds listed in page 9, right upper column, line 1 to page 11, left lower column, line 4 of JP-A-4-121739 can be used in the color developing solution for use in the present invention. Preferred color developing agents for use in especially rapid processing are 2-methyl-4-[N-ethyl-N-(2-hydroxyethyl)amino]aniline, 2-methyl-4-[N-ethyl-N-(3-hydroxypropyl)amino]aniline and 2-methyl-4-[N-ethyl-N-(4-hydroxybutyl)amino]aniline.

These color developing agents are preferably used in an amount of 0.01 to 0.08 mol, more preferably 0.015 to 0.06 mol, and most preferably 0.02 to 0.05 mol per liter (hereinafter also referred to as "L") of the



color developing solution. The replenisher of the color developing solution preferably contains the color developing agent in an amount corresponding to 1.1 to 3 times the above concentration, more preferably 1.3 to 2.5 times the above concentration.

Hydroxylamine can widely be used as a preservative of the color developing solution. When enhanced preserving properties are required, it is preferred to use hydroxylamine derivatives having substituents such as alkyl, hydroxyalkyl, sulfoalkyl and carboxyalkyl groups. Preferred examples thereof include N,N-di(sulfoethyl)hydroxylamine, monomethylhydroxylamine, dimethylhydroxylamine, monoethylhydroxylamine, diethylhydroxylamine and N,N-di(carboxyethyl)hydroxylamine. Of these, N,N-di(sulfoethyl)hydroxylamine is most preferred. Although these may be used in combination with hydroxylamine, it is preferred that one or two or more members thereof be used in place of hydroxylamine.

These preservatives are preferably used in an amount of 0.02 to 0.2 mol, more preferably 0.03 to 0.15 mol, and most preferably 0.04 to 0.1 mol per L of the color developing solution. The replenisher of the color developing solution preferably contains the preservatives in an amount corresponding to 1.1 to 3 times the concentration of the mother liquor (processing tank solution) as in the color developing

agent.

Sulfurous salts are used as tarring preventives for the color developing agent oxidation products in the color developing solution. Sulfurous salts are preferably used in the color developing solution in an amount of 0.01 to 0.05 mol, more preferably 0.02 to 0.04 mol per L. In the replenisher, sulfurous salts are preferably used in an amount corresponding to 1.1 to 3 times the above concentration.

The pH value of the color developing solution preferably ranges from 9.8 to 11.0, more preferably from 10.0 to 10.5. The pH of the replenisher is preferably set for a value 0.1 to 1.0 higher than the above value. Common buffers, such as carbonic acid salts, phosphoric acid salts, sulfosalicylic acid salts and boric acid salts, are used for stabilizing the above pH value.

Although the amount of the replenisher of the color developing solution preferably ranges from 80 to 1300 mL per m<sup>2</sup> of the lightsensitive material, the employment of smaller amount is desirable from the viewpoint of reduction of environmental pollution load. Specifically, the amount of the replenisher more preferably ranges from 80 to 600 mL, most preferably from 80 to 400 mL.

The bromide ion concentration in the color developer is usually 0.01 to 0.06 mol per L. However,

this bromide ion concentration is preferably set at 0.015 to 0.03 mol per L in order to suppress fog and improve discrimination and graininess while maintaining sensitivity. To set the bromide ion concentration in this range, it is only necessary to add bromide ions calculated by the following equation to a replenisher. If C represented by formula below takes a negative value, however, no bromide ions are preferably added to a replenisher.

10           
$$C = A - W/V$$

where C : the bromide ion concentration (mol/L) in a color developer replenisher

A : the target bromide ion concentration (mol/L) in a color developer

15           W : the amount (mol) of bromide ions dissolving into the color developer from 1 m<sup>2</sup> of a light-sensitive material when the sensitive material is color-developed

            V : the replenishment rate (L) of the color developer replenisher for 1 m<sup>2</sup> of the light-sensitive material

20

As a method of increasing the sensitivity when the replenishment rate is decreased or high bromide ion concentration is set, it is preferable to use a development accelerator such as pyrazolidones represented by 1-phenyl-3-pyrazolidone and 1-phenyl-2-methyl-2-hydroxymethyl-3-pyrazolidone, or

25

a thioether compound represented by  
3,6-dithia-1,8-octandiol.

Color reversal film processing solutions used in  
the present invention will be described below.

5           Processing for a color reversal film is described  
in detail in Aztech Ltd., Known Technology No. 6 (1991,  
April 1), page 1, line 5 to page 10, line 5 and page  
15, line 8 to page 24, line 2, and any of the contents  
can be preferably applied.

10           Photographic additives usable in the present  
invention are also described in RDs, and the relevant  
portions are summarized in the following table.

15	Additives	RD17643	RD18716
	1. Chemical sensitizers	page 23	page 648, right column
20	2. Sensitivity increasing agents		do
	3. Spectral sensitizers, super sensitizers	pages 23 - 24	page 648, right column to page 649, right column
25	4. Brighteners	page 24	page 647, right column
30	5. Light absorbents, filter dyes, ultraviolet absorbents	pages 25 - 26	page 649, right column to page 650, left column
35	6. Binders	page 26	page 651, left column
	7. Plasticizers, lubricants	page 27	page 650, right column
40	8. Coating aids, surface active agents	pages 26 - 27	do

	9. Antistatic agents	page 27	do
	10. Matting agents		
5	Additives	RD307105	
	1. Chemical sensitizers	page 866	
10	2. Sensitivity increasing agents		
	3. Spectral sensitizers, super sensitizers	pages 866 - 868	
15	4. Brighteners	page 868	
	5. Light absorbent, filter dye, ultra-violet absorbents	page 873	
20	6. Binder	pages 873 - 874	
	7. Plasticizers, lubricants	page 876	
25	8. Coating aids, surface active agents	pages 875 - 876	
30	9. Antistatic agents	pages 876 - 877	
	10. Matting agent	pages 878 - 879	
35			

Techniques such as a layer arrangement technique, silver halide emulsions, dye forming couplers, functional couplers such as DIR couplers, various additives, and development usable in silver halide photographic light-sensitive materials are described in European Patent No. 0565096A1 (laid open in October 13, 1993) and the patents cited in it, the disclosures of which are incorporated herein by reference. The individual items and the corresponding portions are enumerated below.

1. Layer arrangements: page 61, lines 23 - 35,  
page 61, line 41 - page 62, line 14
2. Interlayers: page 61, lines 36 - 40
3. Interlayer effect donor layers: page 62,  
5 lines 15 - 18
4. Silver halide halogen compositions: page 62,  
lines 21 - 25
5. Silver halide grain crystal habits: page 62,  
lines 26 - 30
- 10 6. Silver halide grain size: page 62, lines 31 - 34
7. Emulsion preparation methods: page 62,  
lines 35 - 40
8. Silver halide grain size distribution: page 62,  
lines 41 - 42
- 15 9. Tabular grains: page 62, lines 43 - 46
10. Internal structures of grains: page 62,  
lines 47 - 53
11. Latent image formation types of emulsions:  
page 62, line 54 - page 63, line 5
- 20 12. Physical ripening and chemical sensitization of  
emulsions: page 63, lines 6 - 9
13. Use of emulsion mixtures: page 63, lines 10 - 13
14. Fogged emulsions: page 63, lines 14 - 31
15. Non-light-sensitive emulsions: page 63,  
25 lines 32 - 43
16. Silver coating amount: page 63, lines 49 - 50
17. Formaldehyde scavengers: page 64, lines 54 - 57

18. Mercapto-based antifoggants: page 65, lines 1 - 2
19. Agents releasing, e.g., fogging agent: page 65,  
lines 3 - 7
20. Dyes: page 65, lines 7 - 10
- 5 21. General color couplers: page 65, lines 11 - 13
22. Yellow, magenta, and cyan couplers: page 65,  
lines 14 - 25
23. Polymer couplers: page 65, lines 26 - 28
24. Diffusing dye forming couplers: page 65,  
10 lines 29 - 31
25. Colored couplers: page 65, lines 32 - 38
26. General functional couplers: page 65,  
lines 39 - 44
27. Bleaching accelerator release couplers: page 65,  
15 lines 45 - 48
28. Development accelerator release couplers: page 65,  
lines 49 - 53
29. Other DIR couplers: page 65, line 54 - page 66,  
line 4
- 20 30. Coupler diffusing methods: page 66, lines 5 - 28
31. Antiseptic agents and mildewproofing agents:  
page 66, lines 29 - 33
32. Types of light-sensitive materials: page 66,  
lines 34 - 36
- 25 33. Light-sensitive layer film thickness and swell  
speed: page 66, line 40 - page 67, line 1
34. Back layers: page 67, lines 3 - 8

- 35. General development processing: page 67,  
lines 9 - 11
- 36. Developers and developing agents: page 67,  
lines 12 - 30
- 5 37. Developer additives: page 67, lines 31 - 44
- 38. Reversal processing: page 67, lines 45 - 56
- 39. Processing solution aperture ratio: page 67,  
line 57 - page 68, line 12
- 40. Development time: page 68, lines 13 - 15
- 10 41. Bleach-fix, bleaching, and fixing: page 68,  
line 16 - page 69, line 31
- 42. Automatic processor: page 69, lines 32 - 40
- 43. Washing, rinsing, and stabilization: page 69,  
line 41 - page 70, line 18
- 15 44. Replenishment and reuse of processing solutions:  
page 70, lines 19 - 23
- 45. Incorporation of developing agent into  
light-sensitive material: page 70, lines 24 - 33
- 46. Development temperature: page 70, lines 34 - 38
- 20 47. Application to film with lens: page 70,  
lines 39 - 41

With respect to the technologies, such as those regarding a bleaching solution, a magnetic recording layer, a polyester support and an antistatic agent,  
25 that are applicable to the silver halide photographic  
lightsensitive material of the present invention and  
with respect to the utilization of the present



invention in Advanced Photo System, etc., reference can be made to US 2002/0042030 A1 (published on April 11, 2002) and patents cited therein. Individual items and the locations where they are described will be listed below.

1. Bleaching solution: page 15 [0206];
2. Magnetic recording layer and magnetic particles: page 16 [0207] to [0213];
3. Polyester support: page 16 [0214] to page 17 [0218];
4. Antistatic agent: page 17 [0219] to [0221];
5. Sliding agent: page 17 [0222];
6. Matte agent: page 17 [0224];
7. Film cartridge: page 17 [0225] to page 18 [0227];
8. Use in Advanced Photo System: page 18 [0228], and [0238] to [0240];
9. Use in lens-equipped film: page 18 [0229]; and
10. Processing by minilab system: page 18 [0230] to [0237].

(Examples)

The present invention will be described in detail below with reference to the following Examples which however in no way limit the scope of the invention.

(Example 1)

Support

A support used in this example was formed by the

following method.

(i) First layer and undercoat layer

5 Glow discharge was performed on the two surfaces of a 90- $\mu\text{m}$  thick polyethylenenaphthalate support at a processing ambient pressure of 26.6 Pa, an  $\text{H}_2\text{O}$  partial pressure in the ambient gas of 75%, a discharge frequency of 30 kHz, an output of 2,500 W, and a processing intensity of 0.5  $\text{kV}\cdot\text{A}\cdot\text{min}/\text{m}^2$ . One surface (back surface) of this support was coated with 5  $\text{mL}/\text{m}^2$  of a coating solution having the following composition as a first layer by using a bar coating method described in JP-B-58-4589, the disclosure of which is incorporated herein by reference.

10 Conductive fine-grain dispersion 50 parts by weight (a water dispersion having an  $\text{SnO}_2/\text{Sb}_2\text{O}_5$  grain concentration of 10%, a secondary aggregate having a primary grain size of 0.005  $\mu\text{m}$  and an average grain size of 0.05  $\mu\text{m}$ )

20	Gelatin	0.5 parts by mass
	Water	49 parts by mass
	Polyglycerolpolyglycidyl ether	0.16 parts by mass
	Poly(polymerization degree 20)	0.1 part by mass
	oxyethylenesorbitanmonolaurate	

25 In addition, after the first layer was formed by coating, the support was wound on a stainless-steel core 20 cm in diameter and heated at 110°C ( $T_g$  of PEN support: 119°C) for 48 hr so as to be given thermal

hysteresis, thereby performing annealing. After that, the side (emulsion surface side) of the support away from the first layer side was coated with 10 mL/m<sup>2</sup> of a coating solution having the following composition as an undercoat layer for emulsions, by using a bar coating method.

	Gelatin	1.01 parts by mass
	Salicylic acid	0.30 parts by mass
	Resorcin	0.40 parts by mass
10	Poly(polymerization degree 10) oxyethylenenonylphenyl ether	0.11 parts by mass
	Water	3.53 parts by mass
	Methanol	84.57 parts by mass
	n-Propanol	10.08 parts by mass

15 Furthermore, second and third layers to be described later were formed in this order on the first layer by coating. Subsequently, the opposite side was coated with multiple layers of a color negative light-sensitive material having a composition to be described later, thereby making a transparent magnetic recording medium having silver halide emulsion layers.

(ii) Second layer (transparent magnetic recording layer)

(1) Dispersion of magnetic substance

25 1,100 parts by mass of a Co-deposited  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> magnetic substance (average long axis length: 0.25  $\mu$ m, S<sub>BET</sub>: 39 m<sup>2</sup>/g, H<sub>c</sub>: 6.56  $\times 10^4$  A/m,  $\sigma_s$ : 77.1 Am<sup>2</sup>/kg,

or: 37.4 Am<sup>2</sup>/kg), 220 parts by mass of water, and  
165 parts by mass of a silane coupling agent  
[3-(poly(polymerization degree 10)oxyethynyl)oxypropyl  
trimethoxysilane] were added and well kneaded for 3 hr  
5 by an open kneader. This coarsely dispersed viscous  
solution was dried at 70°C for 24 hr to remove water and  
heated at 110°C for 1 hr to form surface-treated  
magnetic grains.

These grains were again kneaded for 4 hr by the  
10 following formulation by using an open kneader.

	Above-mentioned surface-treated	855	g
	magnetic grains		
	Diacetylcellulose	25.3	g
	Methylethylketone	136.3	g
15	Cyclohexanone	136.3	g

The resultant material was finely dispersed at  
2,000 rpm for 4 hr by the following formulation by  
using a sand mill (1/4 G sand mill). Glass beads 1 mm  
in diameter were used as media.

20	Above-mentioned kneaded solution	45	g
	Diacetylcellulose	23.7	g
	Methylethylketone	127.7	g
	Cyclohexanone	127.7	g

Furthermore, magnetic substance-containing  
25 intermediate solution was formed by the following  
formulation.

(2) Formation of magnetic substance-containing intermediate solution

Above-mentioned magnetic substance 674 g  
finely dispersed solution

5 Diacetylcellulose solution 24,280 g  
(solid content 4.34%, solvent:  
methylethylketone/cyclohexanone = 1/1)

Cyclohexanone 46 g

10 These materials were mixed, and the mixture was  
stirred by a disperser to form a "magnetic  
substance-containing intermediate solution".

An  $\alpha$ -alumina polishing material dispersion of the present invention was formed by the following formulation.

15 (a) Sumicorundum AA-1.5 (average primary grain size  
1.5  $\mu\text{m}$ , specific surface area 1.3  $\text{m}^2/\text{g}$ )

Formation of grain dispersion

Sumikorandom AA-1.5 152 g

Silane coupling agent KBM 903 0.48 g

20 (manufactured by Shin-Etsu Silicone)

Diacetylcellulose solution 227.52 g

(solid content 4.5%, solvent:

methylethylketone/cyclohexanone = 1/1)

25 The above formulation was finely dispersed at  
800 rpm for 4 hr by using a ceramic-coated sand mill  
(1/4 G sand mill). Zirconia beads 1 mm in diameter  
were used as media.

(b) Colloidal silica grain dispersion (fine grains)

"MEK-ST" manufactured by Nissan Chemical Industries, Ltd. was used.

5 "MEK-ST" was a colloidal silica dispersion containing methylethylketone as a dispersion medium and having an average primary grain size of 0.015  $\mu\text{m}$ . The solid content is 30%.

(3) Formation of second layer coating solution

10	Above-mentioned magnetic substance-	19,053	g
	containing intermediate solution		
	Diacetylcellulose solution	264	g
	(solid content 4.5%, solvent: methylethylketone/cyclohexanone = 1/1)		
15	Colloidal silicon dispersion "MEK-ST"	128	g
	[dispersion b] (solid content 30%)		
	AA-1.5 dispersion [dispersion a]	12	g
	Millionate MR-400 (manufactured by Nippon Polyurethane K.K.) diluted solution	203	g
	(solid content 20%, diluent solvent: methylethylketone/cyclohexanone = 1/1)		
20	Methylethylketone	170	g
	Cyclohexanone	170	g

A coating solution formed by mixing and stirring the above materials was coated in an amount of  
25 29.3 mL/m<sup>2</sup> by using a wire bar. The solution was dried at 110°C. The thickness of the dried magnetic layer was 1.0  $\mu\text{m}$ .

(iii) Third layer (higher fatty acid ester slipping agent-containing layer)

(1) Formation of undiluted dispersion

A solution A presented below was dissolved at 100°C and added to a solution B. The resultant solution mixture was dispersed by a high-pressure homogenizer to form an undiluted dispersion of a slipping agent.

Solution A

	Compound below	399 parts by mass
10	$C_6H_{13}CH(OH)(CH_2)_{10}COOC_{50}H_{101}$	
	Compound below	177 parts by mass
	$n-C_{50}H_{101}O(CH_2CH_2O)_{16}H$	
	Cyclohexanone	830 parts by mass

Solution B

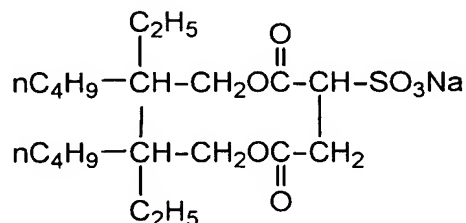
15	Cyclohexanone	8,600 parts by mass
----	---------------	---------------------

(2) Formation of spherical inorganic grain dispersion

A spherical inorganic grain dispersion [c1] was formed by the following formulation.

	Isopropyl alcohol	93.54 parts by mass
20	Silane coupling agent KBM903	5.53 parts by mass
	(manufactured by Shin-Etsu Silicone)	
	compound 1-1: $(CH_3O)_3Si-(CH_2)_3-NH_2$	
	Compound 1	2.93 parts by mass

Compound 1



SEAHOSTAR KEP50 88.00 parts by mass  
(amorphous spherical silica, average grain size  
0.5  $\mu\text{m}$ , manufactured by NIPPON SHOKUBAI Co.,  
Ltd.)

5 The above formulation was stirred for 10 min, and  
the following was further added.

Diacetone alcohol 252.93 parts by mass

Under ice cooling and stirring, the above solution  
was dispersed for 3 hr by using the "SONIFIER450  
10 (manufactured by BRANSON K.K.)" ultrasonic homogenizer,  
thereby completing the spherical inorganic grain  
dispersion c1.

(3) Formation of spherical organic polymer grain  
dispersion

15 A spherical organic polymer grain dispersion [c2]  
was formed by the following formulation.

XC99-A8808 (manufactured by TOSHIBA SILICONE K.K.,  
spherical crosslinked polysiloxane grain,

average grain size 0.9  $\mu\text{m}$ ) 60 parts by mass

20 Methyl ethyl ketone 120 parts by mass

Cyclohexanone 120 parts by mass

(solid content 20%, solvent:

methyl ethyl ketone/cyclohexanone = 1/1)

Under ice cooling and stirring, the above solution  
25 was dispersed for 2 hr by using the "SONIFIER450  
(manufactured by BRANSON K.K.)" ultrasonic homogenizer,  
thereby completing the spherical organic polymer grain



dispersion c2.

(4) Formation of third layer coating solution

The following components were added to 542 g of the aforementioned slipping agent undiluted dispersion to form a third layer coating solution.

5	Diacetone alcohol	5,950	g
	Cyclohexanone	176	g
	Ethyl acetate	1,700	g
	Above-mentioned SEEHOSTA KEP50	53.1	g
10	dispersion [c1]		
	Above-mentioned spherical organic	300	g
	polymer grain dispersion [c2]		
	FC431	2.65g	
	(manufactured by 3M K.K., solid content 50%,		
15	solvent: ethyl acetate)		
	BYK310	5.3	g
	(manufactured by BYK Chemi Japan K.K.,		
	solid content 25 %)		

The above third layer coating solution was coated in an amount of 10.35 mL/m<sup>2</sup> on the second layer, dried at 110°C, and further dried at 97°C for 3 min.

(iv) Coating of light-sensitive layers

The opposite side of the back layers obtained as above was coated with a plurality of layers to make a color negative film.

(Compositions of light-sensitive layers)

The number corresponding to each component

indicates the coating amount in units of g/m<sup>2</sup>. The coating amount of a silver halide is indicated by the amount of silver.

(Sample 101)

5	1st layer (1st antihalation layer)		
	Black colloidal silver	silver	0.074
	Silver iodobromide emulsion grain (average equivalent-sphere diameter 0.07 $\mu$ m, silver iodide content 2 mol%)		
10		silver	0.010
	Gelatin		0.740
	ExM-1		0.068
	ExC-1		0.002
	ExC-3		0.002
15	Cpd-2		0.001
	F-8		0.001
	HBS-1		0.099
	HBS-2		0.013
	2nd layer (2nd antihalation layer)		
20	Black colloidal silver	silver	0.094
	Gelatin		0.667
	ExF-1		0.002
	F-8		0.001
	Solid disperse dye ExF-7		0.100
25	HBS-1		0.066
	ExY-1		0.039

3rd layer (Interlayer)

	ExC-2	0.050
	Cpd-1	0.089
	Polyethylaclyrate latex	0.200
5	HBS-1	0.054
	Gelatin	0.458

4th layer (Low-speed red-sensitive emulsion layer)

	Em-C	silver	0.320
	Em-D	silver	0.414
10	ExC-1		0.354
	ExC-2		0.014
	ExC-3		0.093
	ExC-4		0.193
	ExC-5		0.034
15	ExC-6		0.015
	ExC-8		0.053
	ExC-9		0.020
	Cpd-2		0.025
	Cpd-4		0.025
20	Cpd-7		0.015
	UV-2		0.022
	UV-3		0.042
	UV-4		0.009
	UV-5		0.075
25	HBS-1		0.274
	HBS-5		0.038
	Gelatin		2.757

5th layer (Medium-speed red-sensitive emulsion layer)

	Em-B	silver 1.152
	ExM-5	0.011
	ExC-1	0.304
5	ExC-2	0.057
	ExC-3	0.020
	ExC-4	0.135
	ExC-5	0.012
	ExC-6	0.039
10	ExC-8	0.016
	ExC-9	0.077
	Cpd-2	0.056
	Cpd-4	0.035
	Cpd-7	0.020
15	HBS-1	0.190
	Gelatin	1.1346

6th layer (High-speed red-sensitive emulsion layer)

	Em-A-1	silver 0.932
	ExC-1	0.066
20	ExC-3	0.015
	ExC-6	0.027
	ExC-8	0.114
	ExC-9	0.089
	ExC-10	0.107
25	ExY-3	0.010
	Cpd-2	0.070
	Cpd-4	0.079

	Cpd-7	0.030
	HBS-1	0.314
	HBS-2	0.120
	Gelatin	1.206
5	7th layer (Interlayer)	
	Cpd-1	0.078
	Cpd-6	0.369
	Solid disperse dye ExF-4	0.030
	HBS-1	0.048
10	Polyethylacrylate latex	0.088
	Gelatin	0.739
	8th layer (layer for donating interlayer effect to red-sensitive layer)	
	Em-E	silver 0.408
15	Cpd-4	0.034
	ExM-2	0.121
	ExM-3	0.002
	ExM-4	0.035
	ExY-1	0.018
20	ExY-4	0.038
	ExC-7	0.036
	HBS-1	0.343
	HBS-3	0.006
	HBS-5	0.030
25	Gelatin	0.884
	9th layer (Low-speed green-sensitive emulsion layer)	
	Em-H	silver 0.276

	Em-I	silver	0.238
	Em-J	silver	0.325
	ExM-2		0.344
	ExM-3		0.055
5	ExY-1		0.018
	ExY-3		0.014
	ExC-7		0.004
	HBS-1		0.505
	HBS-3		0.012
10	HBS-4		0.095
	HBS-5		0.055
	Cpd-5		0.010
	Cpd-7		0.020
	Gelatin		1.382
15	10th layer (Medium-speed green-sensitive emulsion layer)		
	Em-G	silver	0.439
	ExM-2		0.046
	ExM-3		0.033
20	ExM-5		0.019
	ExY-3		0.006
	ExC-6		0.010
	ExC-7		0.011
	ExC-8		0.010
25	ExC-9		0.009
	HBS-1		0.046
	HBS-3		0.002

	HBS-4		0.035
	HBS-5		0.020
	Cpd-5		0.004
	Cpd-7		0.010
5	Gelatin		0.446
	11th layer (High-speed green-sensitive emulsion layer)		
	Em-F	silver	0.497
	Em-H	silver	0.286
	ExC-6		0.007
10	ExC-8		0.012
	ExC-9		0.014
	ExM-1		0.019
	ExM-2		0.056
	ExM-3		0.013
15	ExM-4		0.034
	ExM-5		0.039
	ExM-6		0.021
	ExY-3		0.005
	Cpd-3		0.005
20	Cpd-4		0.007
	Cpd-5		0.010
	Cpd-7		0.020
	HBS-1		0.248
	HBS-3		0.003
25	HBS-4		0.094
	HBS-5		0.037
	Polyethylacrylate latex		0.099

	Gelatin		0.950
	12th layer (Yellow filter layer)		
	Cpd-1		0.090
	Solid disperse dye ExF-2		0.070
5	Solid disperse dye ExF-5		0.010
	Oil-soluble dye ExF-6		0.010
	HBS-1		0.055
	Gelatin		0.589
	13th layer (Low-speed blue-sensitive emulsion layer)		
10	Em-M	silver	0.327
	Em-N	silver	0.174
	Em-O	silver	0.097
	ExC-1		0.006
	ExC-3		0.033
15	ExC-7		0.014
	ExY-1		0.088
	ExY-2		0.404
	ExY-4		0.056
	ExY-5		0.404
20	Cpd-2		0.102
	Cpd-3		0.004
	HBS-1		0.337
	HBS-5		0.070
	Gelatin		1.876
25	14th layer (High-speed blue-sensitive emulsion layer)		
	Em-L	silver	0.421
	Em-K	silver	0.421



	ExM-5	0.012
	ExC-1	0.010
	ExY-1	0.041
	ExY-2	0.119
5	ExY-3	0.008
	ExY-4	0.070
	ExY-5	0.120
	Cpd-2	0.074
	Cpd-3	0.001
10	Cpd-7	0.030
	HBS-1	0.122
	Gelatin	0.905
15th layer (1st protective layer)		
Silver iodobromide emulsion grain (average		
15	equivalent-sphere diameter 0.07 $\mu\text{m}$ , silver iodide	
	content 2 mol%)	
	silver	0.278
	UV-1	0.167
	UV-2	0.066
20	UV-3	0.099
	UV-4	0.013
	UV-5	0.160
	F-11	0.008
	S-1	0.077
25	HBS-1	0.175
	HBS-4	0.017
	Gelatin	1.297

16th layer (2nd protective layer)

	H-1	0.400
	B-1 (diameter 1.7 $\mu$ m)	0.050
	B-2 (diameter 1.7 $\mu$ m)	0.150
5	B-3	0.029
	S-1	0.200
	Gelatin	0.748

In addition to the above components, to improve the storage stability, processability, resistance to pressure, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained W-1 to W-11, B-4 to B-6, F-1 to F-19, lead salt, platinum salt, iridium salt, and rhodium salt.

15 Preparation of dispersions of organic solid disperse dyes

ExF-2 in the 12th layer was dispersed by the following method.

	Wet cake (containing 17.6 mass%	2.800 kg
20	of water) of ExF-2	
	Sodium octylphenyldiethoxymethane	0.376 kg
	sulfonate	
	(31 mass% aqueous solution)	
	F-15 (7% aqueous solution)	0.011 kg
25	Water	4.020 kg
	Total	7.210 kg
	(pH was adjusted to 7.2 by NaOH)	

A slurry having the above composition was coarsely dispersed by stirring by using a dissolver. The resultant material was dispersed at a peripheral speed of 10 m/s, a discharge amount of 0.6 kg/min, and a packing ratio of 0.3-mm diameter zirconia beads of 80% by using an agitator mill until the absorbance ratio of the dispersion was 0.29, thereby obtaining a solid disperse dye ExF-2. The average grain size of the fine dye grains was 0.29  $\mu\text{m}$ .

Following the same procedure as above, solid disperse dyes ExF-4 and ExF-7 were obtained. The average grain sizes of the fine dye grains were 0.28 and 0.49  $\mu\text{m}$ , respectively. ExF-5 was dispersed by a microprecipitation dispersion method described in Example 1 of EP549,489A, the disclosure of which is incorporated herein by reference. The average grain size was found to be 0.06  $\mu\text{m}$ .

The grain characteristics of emulsions Em-A-1 and Em-B to Em-O will be listed in Tables 1 to 5. With respect to the emulsions Em-A-1 to Em-O, the optimum gold sensitization, sulfur sensitization and selenium sensitization have been effected by addition of the optimum amount of spectral sensitizing dyes listed in Table 5.

Table 1

Emul- sion name	Layer used	Grain shape	Average equivalent- sphere diameter ( $\mu\text{m}$ )
Em-A-1	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
Em-B	Medium-speed red-sensitive layer	(111) main plane tabular grain	0.69
Em-C	Low-speed red-sensitive layer	(111) main plane tabular grain	0.48
Em-D	Low-speed red-sensitive layer	(111) main plane tabular grain	0.31
Em-E	Layer for donating interlayer effect to red-sensitive layer	(111) main plane tabular grain	0.78
Em-F	High-speed green-sensitive layer	(111) main plane tabular grain	1.00
Em-G	Medium-speed green-sensitive layer	(111) main plane tabular grain	0.74
Em-H	High- and low-speed green- sensitive layers	(111) main plane tabular grain	0.74
Em-I	Low-speed green-sensitive layer	(111) main plane tabular grain	0.55
Em-J	Low-speed green-sensitive layer	(111) main plane tabular grain	0.44
Em-K	High-speed blue-sensitive layer	(111) main plane tabular grain	1.60
Em-L	High-speed blue-sensitive layer	(111) main plane tabular grain	1.30
Em-M	Low-speed blue-sensitive layer	(111) main plane tabular grain	0.81
Em-N	Low-speed blue-sensitive layer	(111) main plane tabular grain	0.40
Em-O	Low-speed blue-sensitive layer	(100) main plane cubic grain	0.21

Table 2

Emulsion name	Average equivalent-circle diameter ( $\mu\text{m}$ )/variation coefficient(%)	Average thickness ( $\mu\text{m}$ )/variation coefficient (%)	Average aspect ratio	Ratio of tabular grains to all the grains in number (%)	Average thickness of core portion ( $\mu\text{m}$ )	Average number of dislocation lines per grain	Ratio of tabular grains satisfying requirement A* to all the grains in number (%)
Em-A-1	1.95/28	0.15/14	13	91	0.12	20	25
Em-B	1.14/35	0.17/15	6.7	90	0.12	15	35
Em-C	0.89/17	0.09/12	10	99	0.07	10	10
Em-D	0.40/20	0.09/9.3	4.5	98	0.07	10	0
Em-E	1.38/30	0.15/13	9.2	90	0.12	20	35
Em-F	1.74/34	0.22/16	7.9	91	0.13	20	10
Em-G	1.23/40	0.18/18	6.8	90	0.12	15	20
Em-H	1.39/25	0.14/11	9.9	91	0.12	20	15
Em-I	0.79/30	0.14/13	5.5	97	0.13	30	0
Em-J	0.53/30	0.17/18	3.2	97	0.10	20	0
Em-K	3.00/25	0.31/21	10	99	0.16	15	0
Em-L	2.20/24	0.34/22	7	98	0.14	20	0
Em-M	1.10/30	0.23/18	4.7	97	0.13	20	5
Em-N	0.55/32	0.13/16	4.6	96	0.11	20	0
Em-O	0.21/20	0.21/20	1	—	—	—	—

\*Requirement A: tabular grains having (111) faces as main planes, the tabular grains: (i) composed of silver iodobromide or silver chloriodobromide; (ii) having an equivalent circle diameter of  $1.0\ \mu\text{m}$  or more and a thickness of  $0.15\ \mu\text{m}$  or less; and (iii) composed of core portions of  $0.1\ \mu\text{m}$  or less thickness free of growth ring structure and composed of silver iodobromide and shell portions having ten or more dislocation lines.

Table 3

Emul- sion name	Average silver iodide content (mol%)/inter- grain variation coefficient (%)	Surface silver iodide content (mol%)	Average silver chloride content (mol%)/inter- grain variation coefficient (%)	Surface silver chloride content (mol%)	Twin plane spacing ( $\mu\text{m}$ )/variation coefficient (%)	(100) face ratio in side planes (%)
Em-A-1	4.5/10	3.90	0	0	0.011/30	20
Em-B	5.5/11	5.00	0	0	0.010/30	30
Em-C	1.5/10	3.70	4.7/8.0	16	0.010/31	25
Em-D	1.1/11	5.00	12/9.0	23	0.009/29	25
Em-E	5.3/10	5.90	0	0	0.012/30	35
Em-F	5.1/10	3.90	0	0	0.012/30	20
Em-G	6.3/13	5.60	0	0	0.010/30	30
Em-H	5.3/14	5.97	0	0	0.011/30	30
Em-I	6.3/12	7.39	0	0	0.016/32	20
Em-J	2.0/14	5.68	0	0	0.016/32	35
Em-K	5.8/7.0	3.88	0	0	0.010/29	40
Em-L	6.1/8.0	5.50	0	0	0.017/33	20
Em-M	6.3/9.0	1.90	0	0	0.019/30	30
Em-N	4.0/10	5.50	0	0	0.020/31	30
Em-O	3.8/9.0	4.50	0	0	—	—

Table 4

Emulsion name	Characteristics of grains accounting for 70% or more of the total projected area	Silver amount ratio of grain structure (%) and halogen composition (listed in order from center of grain); <> indicates epitaxial junction
Em-A-1	(111) main plane tabular grain	(11%)AgBr/(35%)AgBr <sub>97</sub> I <sub>3</sub> /(18%)AgBr/(9%)AgBr <sub>62</sub> I <sub>38</sub> /(27%)AgBr
Em-B	(111) main plane tabular grain	(7%)AgBr/(31%)AgBr <sub>97</sub> I <sub>3</sub> /(16%)AgBr/(12%)AgBr <sub>62</sub> I <sub>38</sub> /(34%)AgBr
Em-C	(111) main plane tabular grain	(1%)AgBr/(77%)AgBr <sub>99</sub> I <sub>1</sub> /(9%)AgBr <sub>95</sub> I <sub>5</sub> /(13%) <AgBr <sub>63</sub> Cl <sub>35</sub> I <sub>2</sub> >
Em-D	(111) main plane tabular grain	(57%)AgBr/(14%)AgBr <sub>96</sub> I <sub>4</sub> /(29%) <AgBr <sub>57</sub> Cl <sub>41</sub> I <sub>2</sub> >
Em-E	(111) main plane tabular grain	(13%)AgBr/(36%)AgBr <sub>97</sub> I <sub>3</sub> /(7%)AgBr/(11%)AgBr <sub>62</sub> I <sub>38</sub> /(33%)AgBr
Em-F	(111) main plane tabular grain	(11%)AgBr/(35%)AgBr <sub>97</sub> I <sub>3</sub> /(18%)AgBr/(4%)AgI/(32%)AgBr
Em-G	(111) main plane tabular grain	(7%)AgBr/(31%)AgBr <sub>97</sub> I <sub>3</sub> /(15%)AgBr/(14%)AgBr <sub>62</sub> I <sub>38</sub> /(33%)AgBr
Em-H	(111) main plane tabular grain	(14%)AgBr/(36%)AgBr <sub>97</sub> I <sub>3</sub> /(7%)AgBr/(11%)AgBr <sub>62</sub> I <sub>38</sub> /(32%)AgBr
Em-I	(111) main plane tabular grain	(15%)AgBr/(44%)AgBr <sub>97</sub> I <sub>3</sub> /(11%)AgBr/(5%)AgI/(25%)AgBr
Em-J	(111) main plane tabular grain	(60%)AgBr/(2%)AgI/(38%)AgBr
Em-K	(111) main plane tabular grain	(68%)AgBr <sub>93</sub> I <sub>7</sub> /(21%)AgBr/(1%)AgI/(10%)AgBr
Em-L	(111) main plane tabular grain	(8%)AgBr/(10%)AgBr <sub>95</sub> I <sub>5</sub> /(52%)AgBr <sub>93</sub> I <sub>7</sub> /(11%)AgBr/(2%)AgI/(17%)AgBr
Em-M	(111) main plane tabular grain	(12%)AgBr/(43%)AgBr <sub>90</sub> I <sub>10</sub> /(14%)AgBr/(2%)AgI/(29%)AgBr
Em-N	(111) main plane tabular grain	(58%)AgBr/(4%)AgI/(38%)AgBr
Em-O	(111) main plane tabular grain	(6%)AgBr/(94%)AgBr <sub>96</sub> I <sub>4</sub>

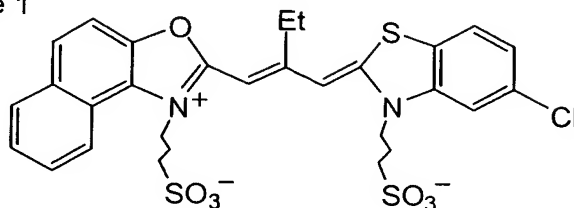
Table 5

Emulsion name	Sensitizing dye	Dopant
Em-A-1	1, 3, 4	$K_2IrCl_6, K_4Fe(CN)_6$
Em-B	2, 3, 4	$K_2IrCl_6, K_2IrCl_5(H_2O), K_4Ru(CN)_6$
Em-C	1, 3, 4	$K_2IrCl_6, K_4Fe(CN)_6$
Em-D	1, 3, 4	$K_2IrCl_6, K_4Fe(CN)_6$
Em-E	5, 10	$K_4Fe(CN)_6$
Em-F	5, 6, 9	$K_4Ru(CN)_6$
Em-G	5, 6, 9	$K_2IrCl_6, K_4Fe(CN)_6$
Em-H	5, 6, 7, 8, 9	$K_2IrCl_6, K_4Fe(CN)_6$
Em-I	6, 8, 9	$K_2IrCl_6$
Em-J	5, 6, 7	$K_2IrCl_6, K_4Fe(CN)_6$
Em-K	14	—
Em-L	12	—
Em-M	14	—
Em-N	12, 13	—
Em-O	11, 13	$K_2IrCl_6$



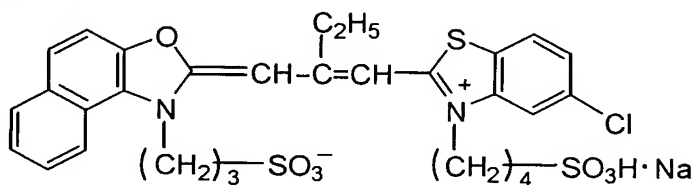
The sensitizing dyes described in Table 5 will be shown below.

Sensitizing dye 1

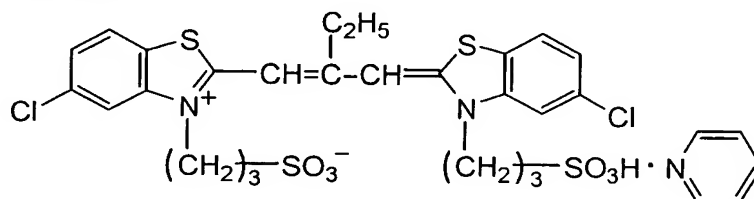


5

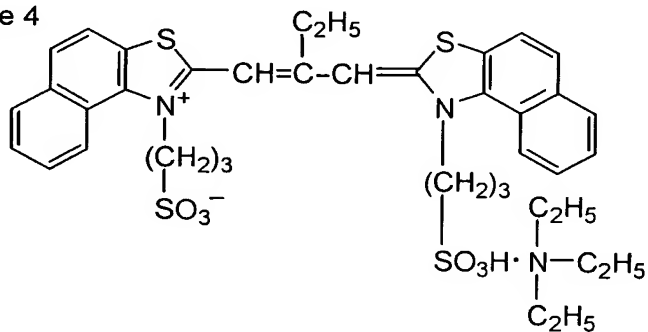
Sensitizing dye 2



Sensitizing dye 3

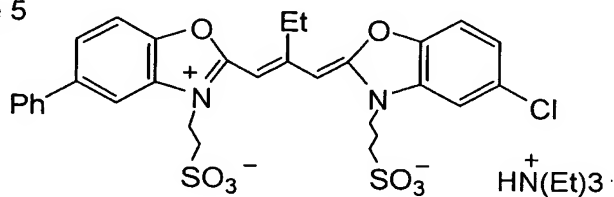


Sensitizing dye 4

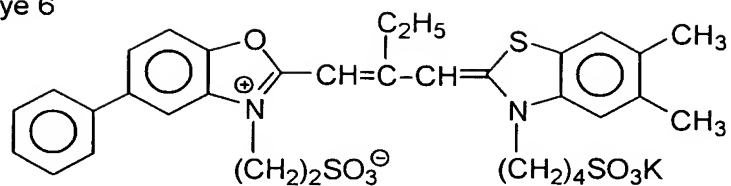


10

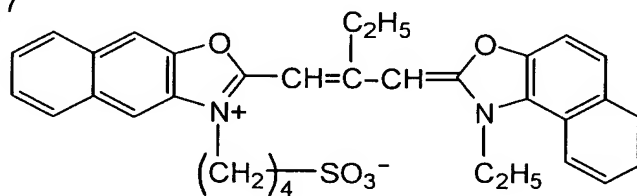
Sensitizing dye 5



Sensitizing dye 6

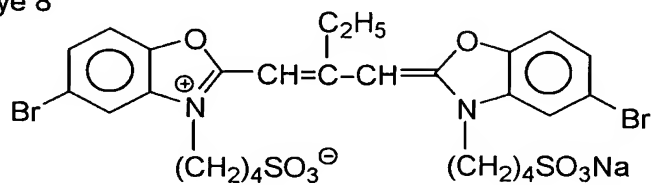


Sensitizing dye 7

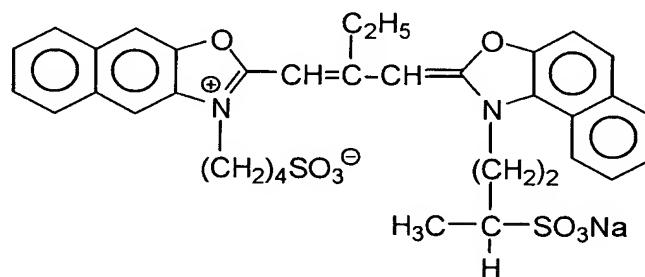


5

Sensitizing dye 8

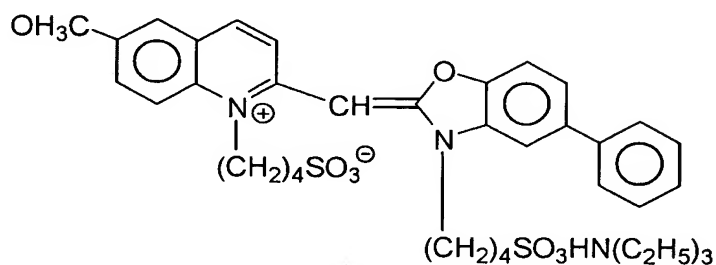


Sensitizing dye 9

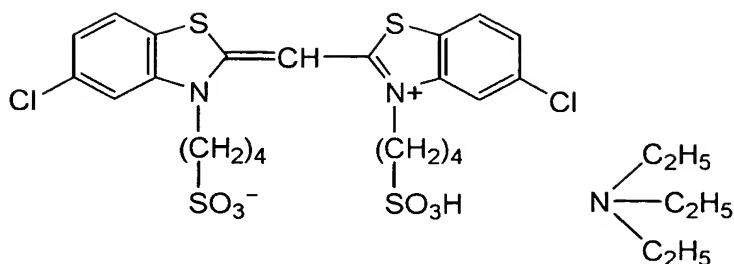


10

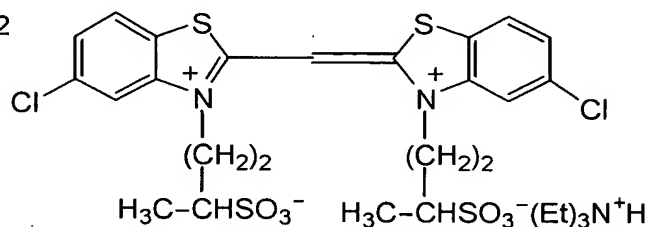
Sensitizing dye 10



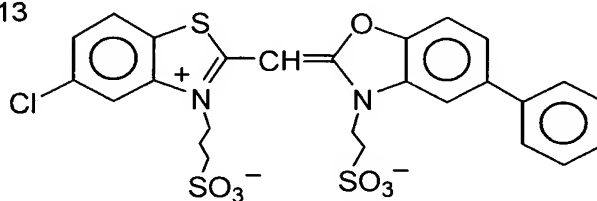
Sensitizing dye 11



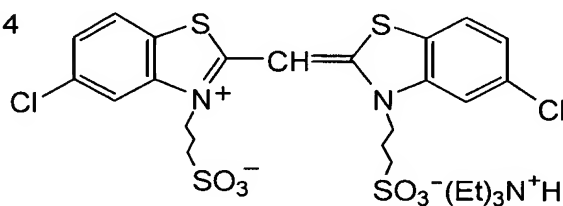
Sensitizing dye 12



Sensitizing dye 13



Sensitizing dye 14



In the preparation of tabular grains, low-molecular-weight gelatins have been used in accordance with Examples of JP-A-1-158426.

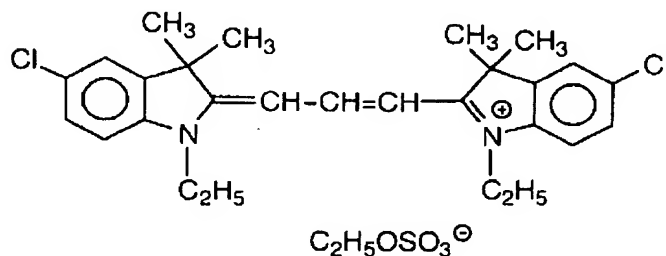
With respect to the emulsions Em-K to Em-N, reduction sensitization thereof has been carried out at the time of grain formation.

With respect to the emulsion Em-H, dislocation has been introduced with the use of iodide ion release agent in accordance with Examples of JP-A-6-11782.

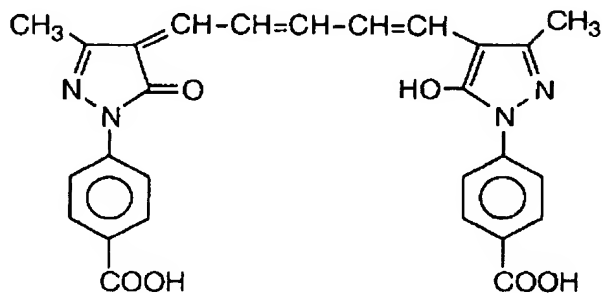
With respect to the emulsion Em-E, dislocation has been introduced with the use of silver iodide fine grains having been prepared just before addition in a separate chamber equipped with magnetic coupling induction type agitator as described in JP-A-10-43570.

The compounds used in the individual layers will be shown below.

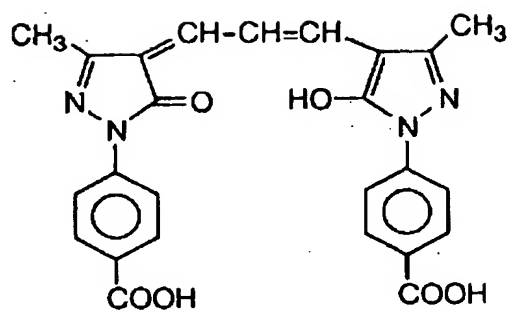
ExF-1



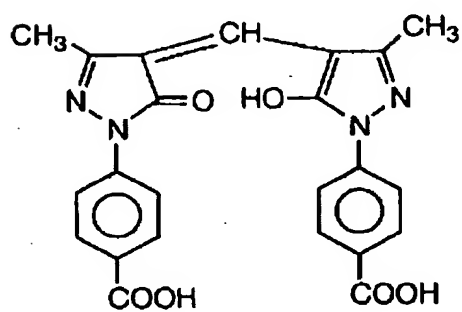
ExF-2



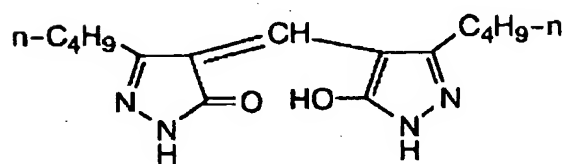
ExF-4



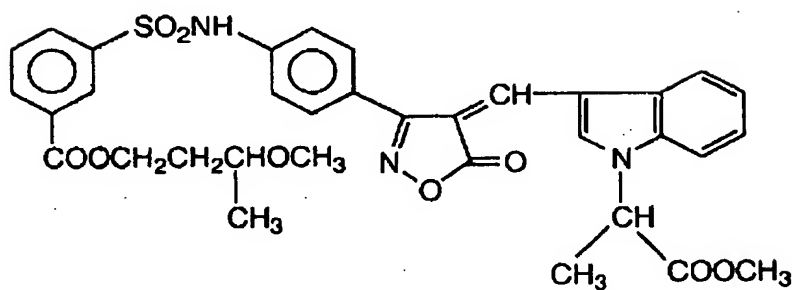
ExF-5



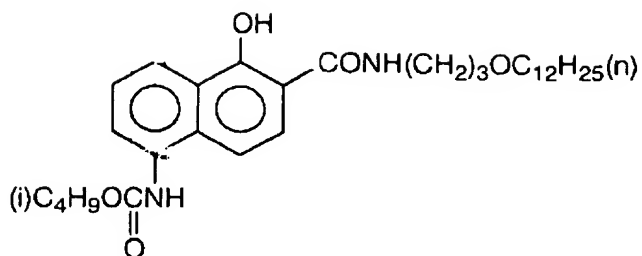
ExF-6



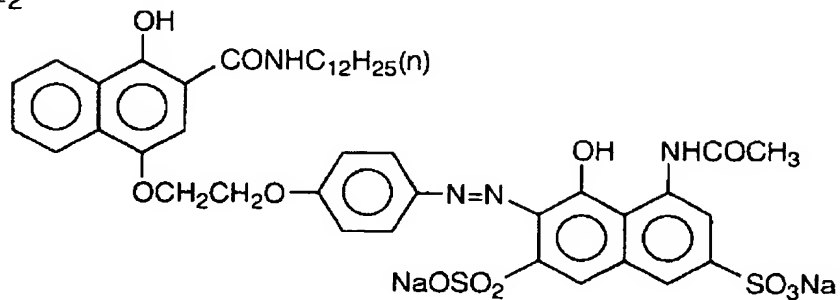
ExF-7



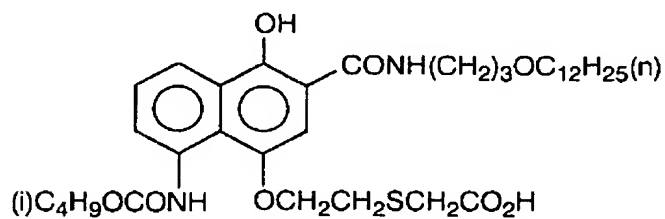
ExC-1



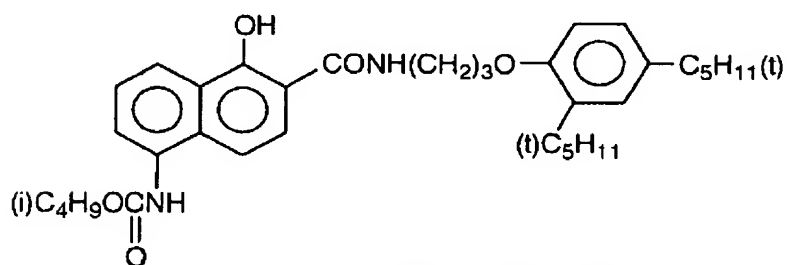
ExC-2



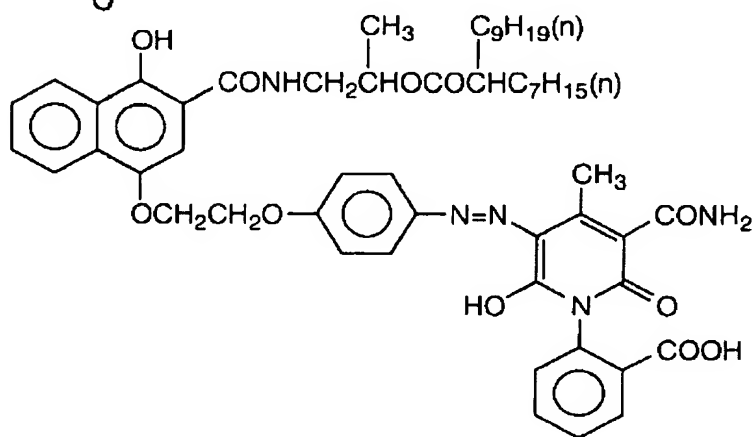
ExC-3



ExC-4

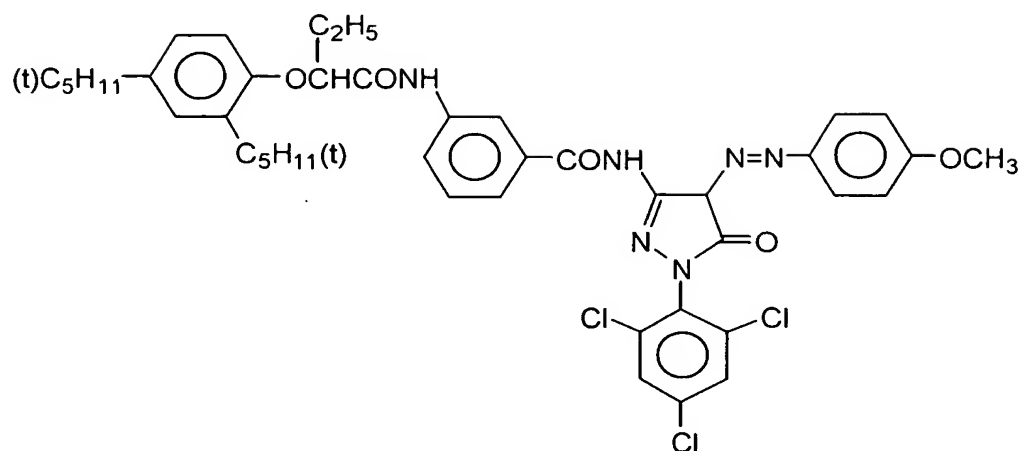


ExC-5

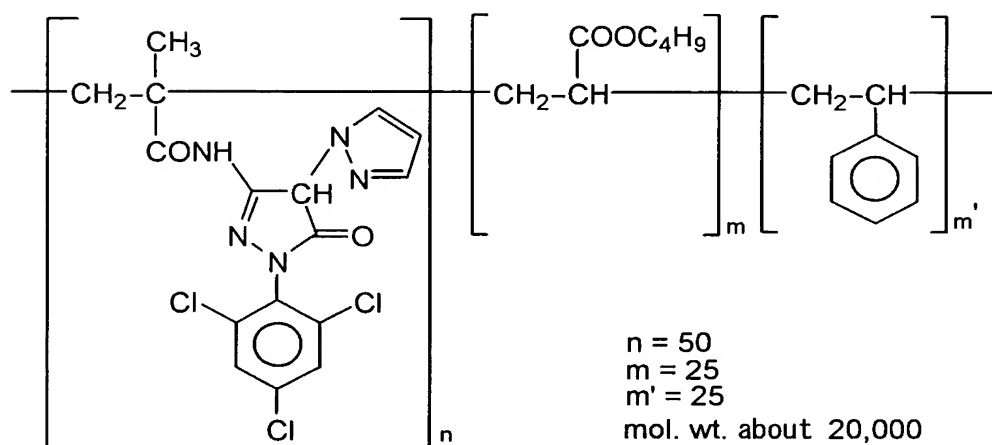


CCCC1=NN(C(=S)N1)CCOC(=O)c2cc(O)c3ccccc23C(=O)Nc4ccccc4OC14H29(n)CCCCCCCCCCCCN(C(=O)C1=NC2=CC(=CC=C2C(=O)OC3=CC=CC=C3)N1)c4c(O)c(cc5ccccc45)C(=O)Nc6ccccc6OCCC(C)COC(=O)Nc1ccc2c(c1)c(O)c(C(=O)NCCCCOc3ccc(cc3)C(C)(C)C)cc2SCCC(=O)OCC(C)COC(=O)Nc1ccc2c(c1)c(c3ccccc23)Oc4cc(=O)n(CCCCOc5ccc(cc5)C(C)(C)CC)cc4SCCCC(=O)OCCCCNC(=O)c1c(O)c(OCCSC(=O)OCCCCCCCCCCCC)cc2c(NC(=O)C(C)C)ccc12

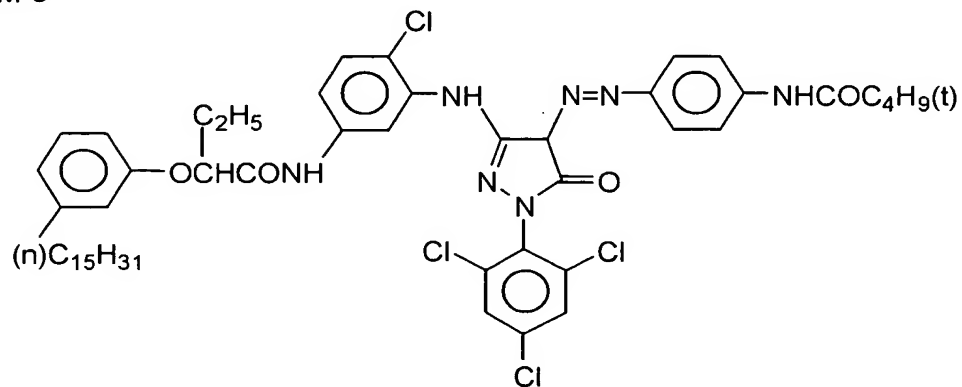
ExM-1



ExM-2

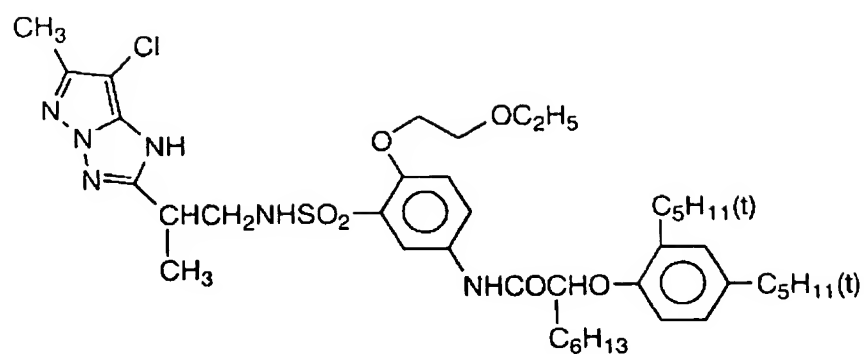


ExM-3

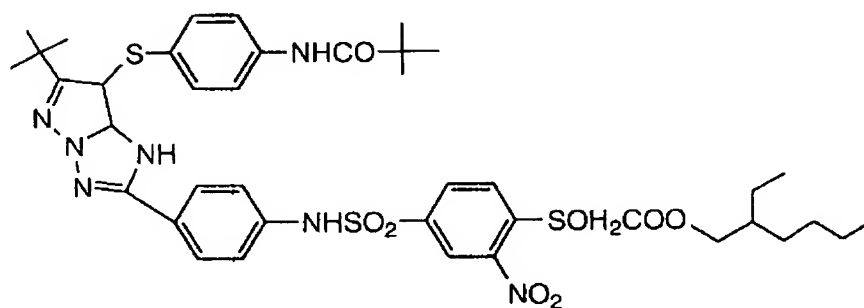




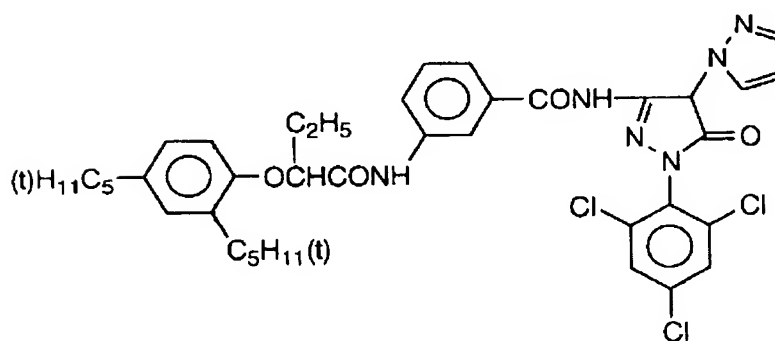
ExM-4



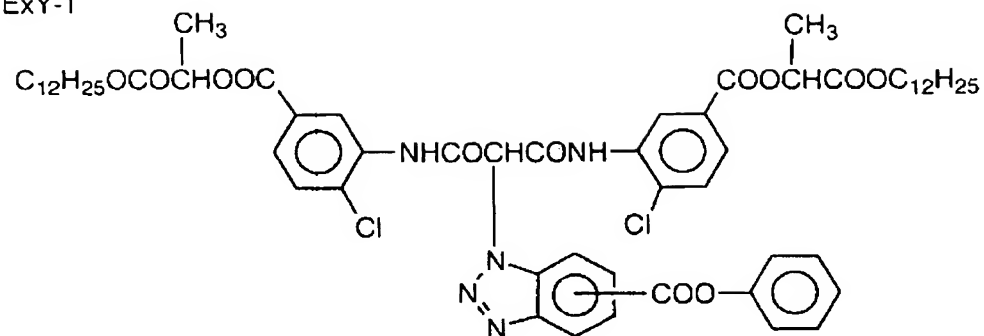
ExM-5



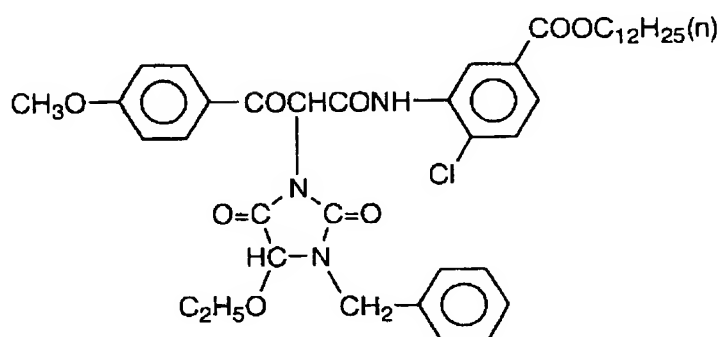
ExM-6



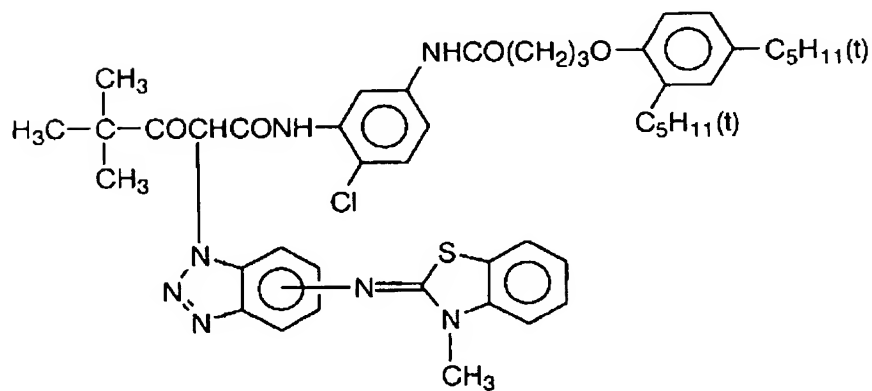
ExY-1



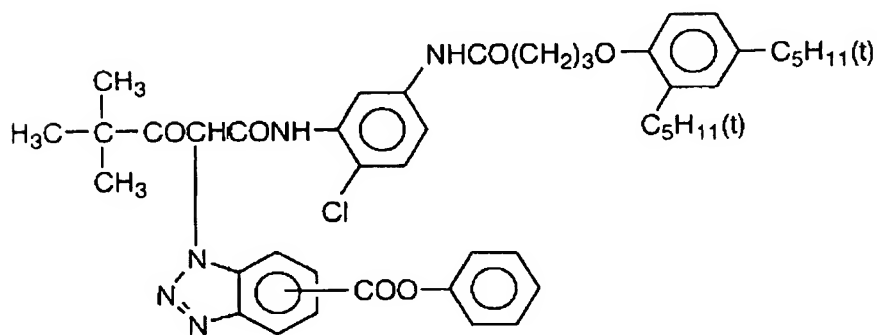
ExY-2



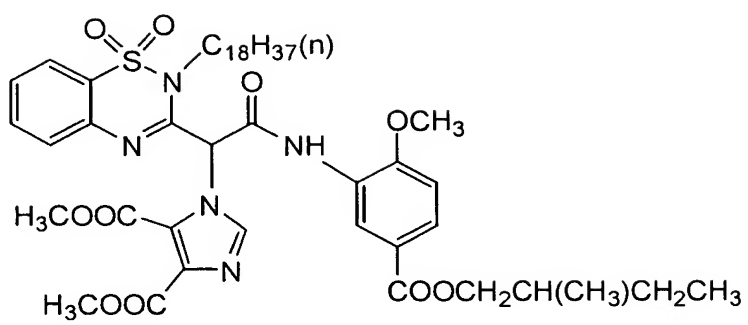
ExY-3

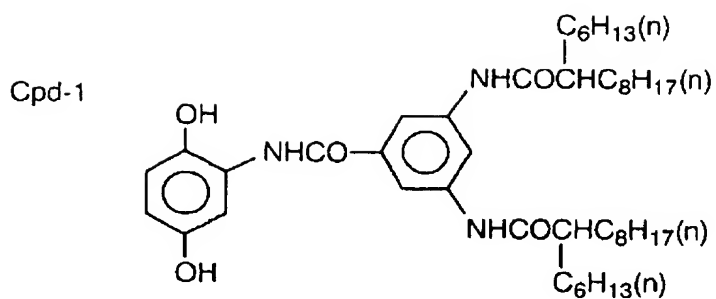


ExY-4

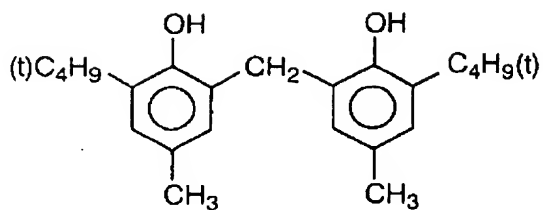


ExY-5

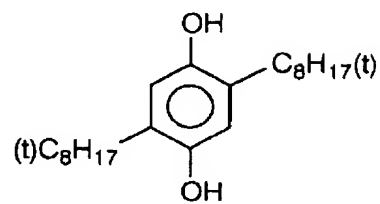




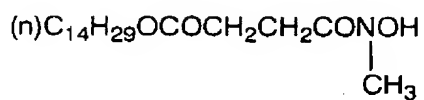
Cpd-2



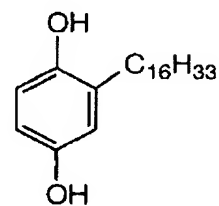
Cpd-3



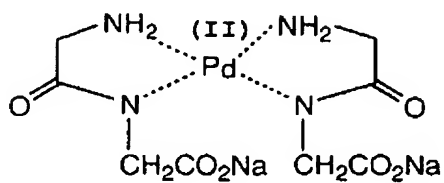
Cpd-4



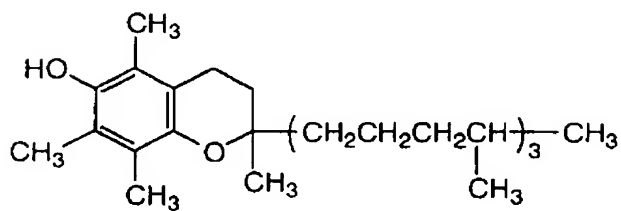
Cpd-5



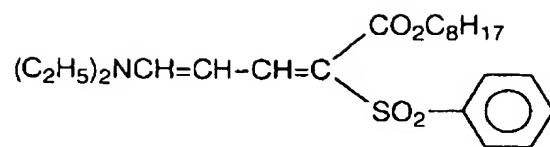
Cpd-6



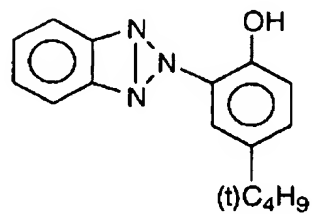
Cpd-7



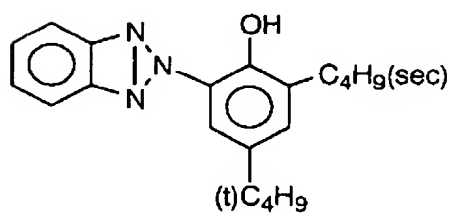
UV-1



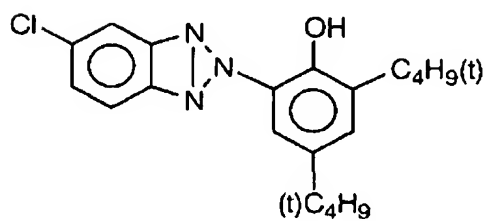
UV-2



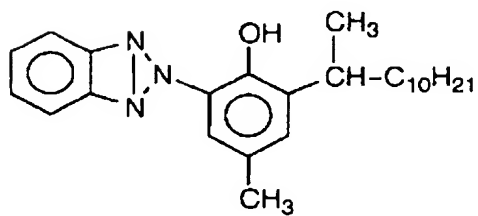
UV-3



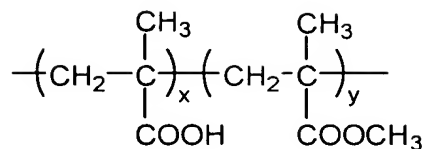
UV-4



UV-5



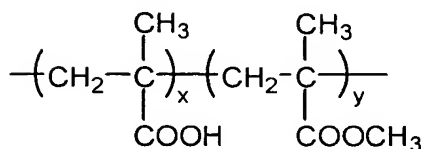
B-1



$x/y=10/90$  (mass ratio)

Weight-average molecular weight: about 35,000

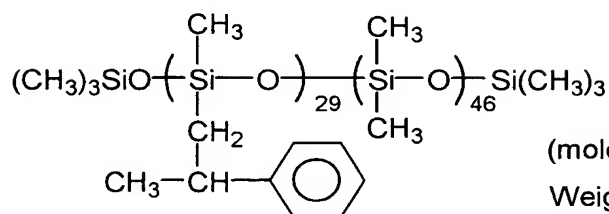
B-2



$x/y=40/60$  (mass ratio)

Weight-average molecular weight: about 20,000

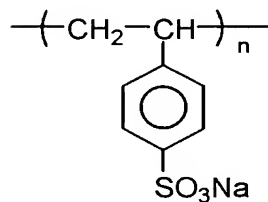
B-3



(mole ratio)

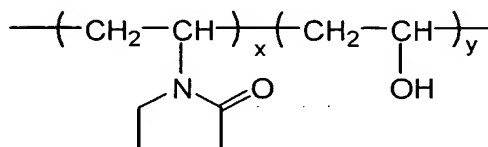
Weight-average molecular weight: about 8,000

B-4



Weight-average molecular weight: about 750,000

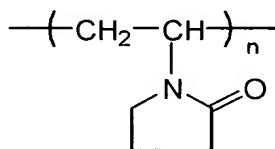
B-5



$x/y=70/30$  (mass ratio)

Weight-average molecular weight: about 17,000

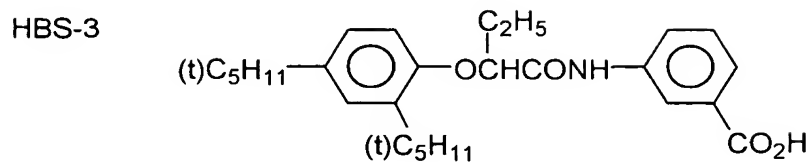
B-6



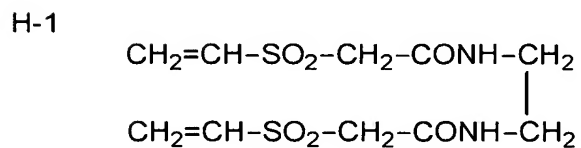
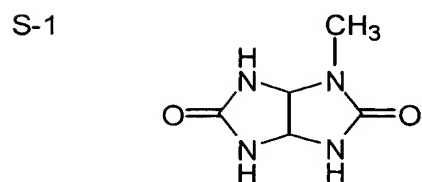
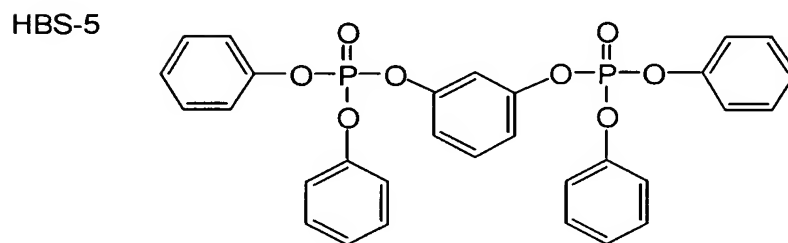
Weight-average molecular weight: about 10,000

HBS-1 Tricresyl phosphate

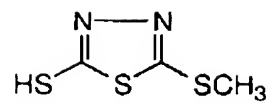
HBS-2 Di-n-butyl phthalate



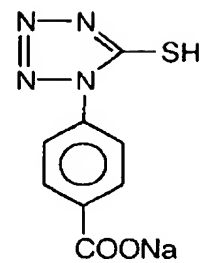
HBS-4 Tri (2-ethylhexyl) phosphate



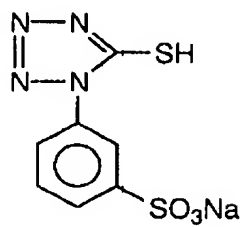
F-1



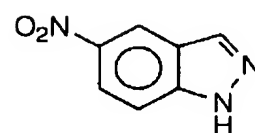
F-2



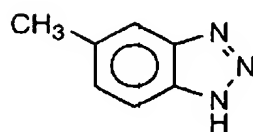
F-3



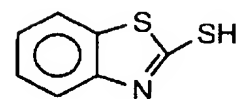
F-4



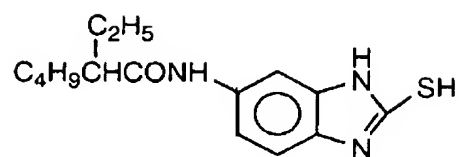
F-5



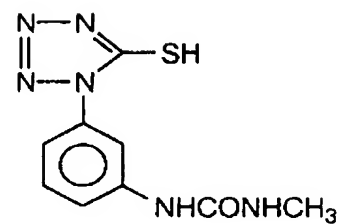
F-6



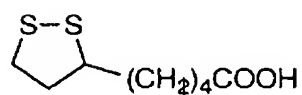
F-7



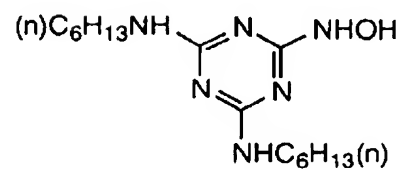
F-8



F-9

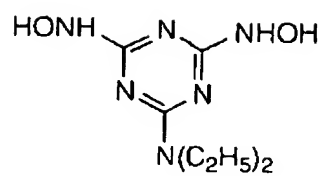


F-10

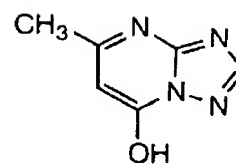




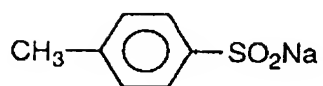
F-11



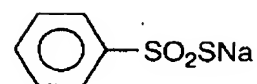
F-12



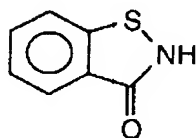
F-13



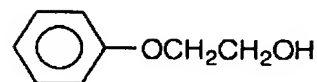
F-14



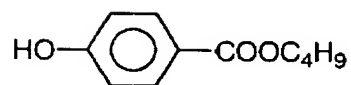
F-15



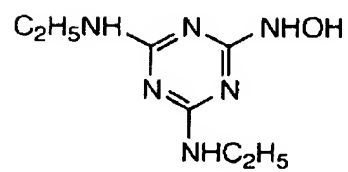
F-16



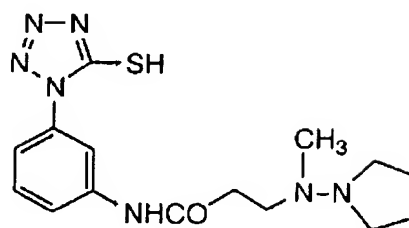
F-17

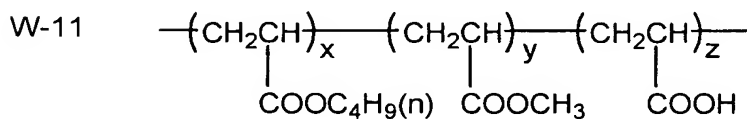
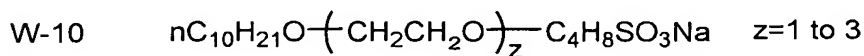
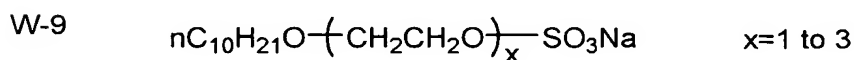
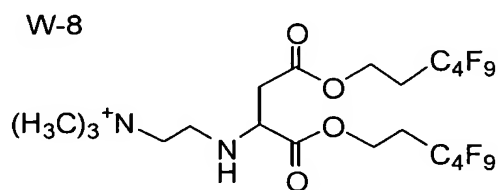
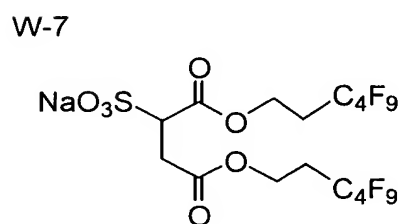
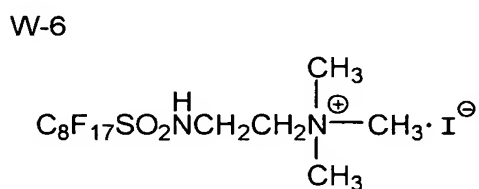
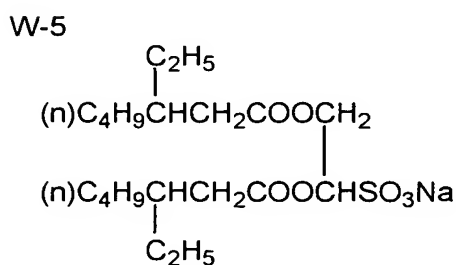
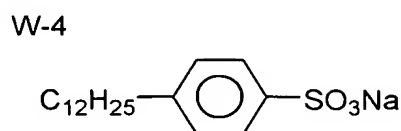
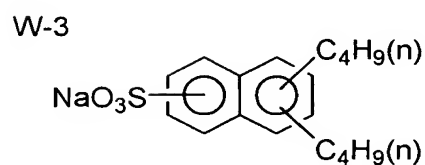
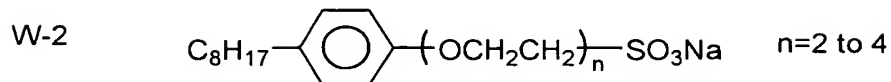
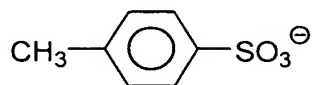
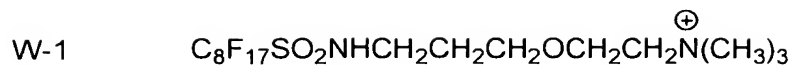


F-18



F-19





$x/y/z = 20/60/20$   
(mass ratio)

Weight-average molecular weight :  
about 36,000

The thus obtained silver halide color photographic

lightsensitive material is referred to as sample 101.

(Samples 102 to 113)

Samples 102 to 113 were prepared by replacing the emulsion Em-A-1 of the 6th layer of the sample 101 as indicated in Table 6 and by adding compounds of the present invention to the 6th layer as indicated in Table 6. The characteristics of emulsions Em-A-2 to Em-A-6 are listed in Table 6.

Table 6

Sample	Emulsion name	Layer used	Grain shape	Average equivalent-sphere diameter ( $\mu\text{m}$ )
101	Em-A-1	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
102	Em-A-1	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
103	Em-A-2	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
104	Em-A-3	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
105	Em-A-2	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
106	Em-A-4	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
107	Em-A-4	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
108	Em-A-4	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
109	Em-A-4	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
110	Em-A-5	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
111	Em-A-5	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
112	Em-A-6	High-speed red-sensitive layer	(111) main plane tabular grain	0.95
113	Em-A-6	High-speed red-sensitive layer	(111) main plane tabular grain	0.95

(Continued)

Table 6

Sample	Average equivalent-circle diameter ( $\mu\text{m}$ ) / variation coefficient (%)	Average thickness ( $\mu\text{m}$ ) / variation coefficient (%)	Average aspect ratio	Ratio of tabular grains to all the grain in number (%)	Average thickness of core portion ( $\mu\text{m}$ )
101	1.95/28	0.15/14	13	97	0.12
102	1.95/28	0.15/14	13	97	0.12
103	2.10/30	0.13/14	16	97	0.10
104	2.10/30	0.13/14	16	97	0.10
105	2.10/30	0.13/14	16	97	0.10
106	2.20/32	0.12/14	18	97	0.09
107	2.20/32	0.12/14	18	97	0.09
108	2.20/32	0.12/14	18	97	0.09
109	2.20/32	0.12/14	18	97	0.09
110	1.95/28	0.15/14	13	97	0.10
111	1.95/28	0.15/14	13	97	0.10
112	1.83/27	0.17/14	11	97	0.10
113	1.83/27	0.17/14	11	97	0.10

(Continued)

Table 6

Sample	Average number of dislocation lines per grain	Ratio of tabular grains satisfying requirement A* to all the grains in number (%)	Compound of the present invention (0.156g/m <sup>2</sup> )	Relative sensitivity	Graininess	Remark
101	20	25	No	100	100	Comp.
102	20	25	HET3	105	100	Comp.
103	20	40	No	101	100	Comp.
104	5	30	HET3	105	101	Comp.
105	20	60	HET3	120	99	Inv.
106	20	80	HET3	130	99	Inv.
107	20	80	(2)	150	99	Inv.
108	20	80	(59)	160	99	Inv.
109	20	80	(60)	145	99	Inv.
110	20	50	No	100	100	Comp.
111	20	50	HET3	115	99	Inv.
112	20	40	No	97	100	Comp.
113	20	40	HET3	105	99	Comp.

\*Requirement A: tabular grains having (111) faces as main planes, the tabular grains: (i) composed of silver iodobromide or silver chloriodobromide; (ii) having an equivalent circle diameter of 1.0  $\mu\text{m}$  or more and a thickness of 0.15  $\mu\text{m}$  or less; and (iii) composed of core portions of 0.1  $\mu\text{m}$  or less thickness free of growth ring structure and composed of silver iodobromide and shell portions having ten or more dislocation lines.

The development was done as follows by using an automatic processor FP-360B manufactured by Fuji Photo Film Co., Ltd. Note that the processor was remodeled so that the overflow solution of the bleaching bath was not carried over to the following bath, but all of it was discharged to a waste fluid tank. The FP-360B processor was loaded with evaporation compensation means described in Journal of Technical Disclosure No. 94-4992.

The processing steps and the processing solution compositions are presented below.

(Processing steps)

Step	Time	Temperature	Replenishment rate*	Tank volume
Color development	3 min 5 sec	37.8°C	20 mL	11.5L
Bleaching	50 sec	38.0°C	5 mL	5L
Fixing (1)	50 sec	38.0°C	-	5L
Fixing (2)	50 sec	38.0°C	8 mL	5L
Washing	30 sec	38.0°C	17 mL	3L
Stabilization (1)	20 sec	38.0°C	-	3L
Stabilization (2)	20 sec	38.0°C	15 mL	3L
Drying	1 min 30 sec	60°C		

\*The replenishment rate was per 1.1m of a 35-mm wide sensitized material (equivalent to one 24 Ex. 1)

The stabilizer and the fixing solution were counterflowed in the order of (2) → (1), and all of

the overflow of the washing water was introduced to the fixing bath (2). Note that the amounts of the developer carried over to the bleaching step, the bleaching solution carried over to the fixing step, and the fixer carried over to the washing step were 2.5 mL, 2.0 mL and 2.0 mL per 1.1m of a 35-mm wide sensitized material, respectively. Note also that each crossover time was 6 sec, and this time was included in the processing time of each preceding step.

The opening area of the above processor for the color developer and the bleaching solution were 100 cm<sup>2</sup> and 120 cm<sup>2</sup>, respectively, and the opening areas for other solutions were about 100 cm<sup>2</sup>.

The compositions of the processing solutions are presented below.

(Color developer)	[Tank solution] (g)	[Replenisher] (g)
Diethylenetriamine pentaacetic acid	3.0	3.0
Disodium catecohl-3,5- disulfonate	0.3	0.3
Sodium sulfite	3.9	5.3
Potassium carbonate	39.0	39.0
Disodium-N,N-bis (2-sulfonatoethyl) hydroxylamine	1.5	2.0
Potassium bromide	1.3	0.3
Potassium iodide	1.3mg	-
4-hydroxy-6-methyl-1,3,3a,7 tetrazaindene	0.05	-



	Hydroxylamine sulfate	2.4	3.3
5	2-methyl-4-[N-ethyl-N-( $\beta$ -hydroxyethyl)amino] aniline sulfate	4.5	6.5
	Water to make	1.0L	1.0L
10	pH (adjusted by potassium hydroxide and surfuric acid)	10.05	10.18
	(Bleaching solution)	[Tank solution] (g)	[Replenisher] (g)
15	Ferric ammonium 1,3- diaminopropanetetra acetate monohydrate	113	170
20	Ammonium bromide	70	105
	Ammonium nitrate	14	21
25	Succinic acid	34	51
	Maleic acid	28	42
	Water to make	1.0L	1.0L
30	pH (adjusted by ammonia water) (Fixer (1) Tank solution)	4.6	4.0
35	A 5:95 mixture (v/v) of the above bleaching tank solution and the below fixing tank solution pH 6.8		
	(Fixer (2))	[Tank solution] (g)	[Replenisher] (g)
40	Ammonium thiosulfate (750 g/L)	240 mL	720 mL
45	Imidazole	7	21
	Ammonium Methanthiosulfonate	5	15
50	Ammonium Methanesulfinat	10	30
	Ethylenediamine	13	39

tetraacetic acid

	Water to make	1L	1L
5	pH (adjusted by ammonia water and acetic acid)	7.4	7.45
	(Washing water)		

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/L or less. Subsequently, 20 mg/L of sodium isocyanuric acid dichloride and 150 mg/L of sodium sulfate were added. The pH of the solution ranged from 6.5 to 7.5.

	(Stabilizer)	common to tank solution and replenisher	(g)
20	Sodium p-toluenesulfinate		0.03
	Polyoxyethylene-p-monononyl phenylether		0.2
25	(average polymerization degree 10)		
	1,2-benzisothiazoline-3-on sodium		0.10
	Disodium ethylenediamine tetraacetate		0.05
30	1,2,4-triazole		1.3
	1,4-bis(1,2,4-triazole-1-ylmethyl) piperazine		0.75
35	Water to make		1.0 L
	pH		8.5

(Estimation 1 sensitivity)

The obtained samples were sequentially subjected to continuous wedge exposure for 1/100 sec through

gelatin filter SC-39 manufactured by Fuji Photo Film Co., Ltd., color development processing described above and determination of sensito-curves, from which the photographic speed (S0.2Y) thereof at cyan density fog + 0.2 was estimated. Respective values indicated are in terms of the speed relative to that of the sample 101. The greater the value, the higher the speed and thus the greater the preference.

(Estimation 2 graininess)

The above samples were subjected to uniform exposure with a light intensity capable of realizing a density of fog density plus 0.2 and to the above development processing. After the development processing, the graininess was measured by the method described on page 619 of "The Theory of the Photographic Process" published by Macmillan.

It is apparent from Table 6 that the silver halide photographic lightsensitive materials of the present invention exhibit high photographic speed and are excellent in graininess.

(Example 2)

The thickness of the protective layer of the sample 101 was 3.5  $\mu\text{m}$ . Samples 201 to 217 were prepared by regulating the amounts of gelatin used in the 15th layer and 16th layer of the sample 101 so that the thickness of the protective layer became 2.5  $\mu\text{m}$  or 1.5  $\mu\text{m}$ , by replacing the emulsion Em-A-1 of the 6th

layer with emulsions Em-A-4 to Em-A-6 specified in Table 6, and by adding compounds of the present invention to the 6th layer. The constitution particulars thereof will be listed in Table 7.

5           (Estimation 1   sensitivity)

The estimation was effected in the same manner as in Example 1.

(Estimation 2   graininess)

10           The estimation was effected in the same manner as in Example 1.

(Estimation 3   sharpness)

15           The obtained samples were sequentially subjected to 1/100 sec exposure through gelatin filter SC-39 manufactured by Fuji Photo Film Co., Ltd. so as to effect white exposure writing of a pattern for MTF estimation and to the above color development processing. The sharpness of cyan density was expressed in terms of value relative to that of the sample 201. The greater the value, the higher the sharpness and thus the greater the preference.

20           Estimation results will be listed in Table 7. It is apparent from the results that the silver halide color photographic lightsensitive material which exhibits high photographic speed and is excellent in graininess and sharpness can be obtained by the combination according to the present invention.

Table 7

Sample	Emulsion name	Layer used	Ratio of tabular grains satisfying requirement A* to all the grains in number (%)
201	Em-A-1	High-speed red-sensitive layer	25
202	Em-A-1	High-speed red-sensitive layer	25
203	Em-A-1	High-speed red-sensitive layer	25
204	Em-A-1	High-speed red-sensitive layer	25
205	Em-A-4	High-speed red-sensitive layer	80
206	Em-A-4	High-speed red-sensitive layer	80
207	Em-A-4	High-speed red-sensitive layer	80
208	Em-A-4	High-speed red-sensitive layer	80
209	Em-A-4	High-speed red-sensitive layer	80
210	Em-A-4	High-speed red-sensitive layer	80
211	Em-A-4	High-speed red-sensitive layer	80
212	Em-A-5	High-speed red-sensitive layer	50
213	Em-A-5	High-speed red-sensitive layer	50
214	Em-A-5	High-speed red-sensitive layer	50
215	Em-A-5	High-speed red-sensitive layer	50
216	Em-A-6	High-speed red-sensitive layer	40
217	Em-A-6	High-speed red-sensitive layer	40

(Continued)

Table 7

Sample	Compound of the present invention (0.156g/m <sup>2</sup> )	Sam of protective layer thickness (μm)	Relative sensitivity	Graininess	Relative sharpness	Remark
201	No	3.5	100	100	100	Comp.
202	HET3	3.5	105	100	100	Comp.
203	No	2.5	101	100	107	Comp.
204	HET3	2.5	105	100	105	Comp.
205	No	3.5	110	99	92	Comp.
206	HET3	3.5	130	99	93	Inv.
207	No	2.5	118	99	109	Inv.
208	HET3	1.5	150	99	120	Inv.
209	(2)	1.5	168	99	121	Inv.
210	(59)	1.5	177	99	118	Inv.
211	(60)	1.5	163	99	119	Inv.
212	No	3.5	100	100	100	Comp.
213	HET3	3.5	115	100	101	Inv.
214	No	1.5	112	100	117	Inv.
215	HET3	1.5	125	100	115	Inv.
216	No	3.5	97	100	101	Comp.
217	HET3	1.5	105	99	103	Comp.

\*Requirement A: tabular grains having (111) faces as main planes, the tabular grains: (i) composed of silver iodobromide or silver chloriodobromide; (ii) having an equivalent circle diameter of 1.0 μm or more and a thickness of 0.15 μm or less; and (iii) composed of core portions of 0.1 μm or less thickness free of growth ring structure and composed of silver iodobromide and shell portions having ten or more dislocation lines.

(Example 3)

Emulsion of the present invention having the same average equivalent sphere diameter as in the emulsion Em-B was produced. This emulsion satisfied all the requirements for the emulsion of the present invention. The emulsion Em-B of the 5th layer (medium-speed red-sensitive emulsion layer) of the sample 101 was replaced with this emulsion, and compound HET-3 of the present invention was added to the 5th layer (medium-speed red-sensitive emulsion layer) in an amount of 0.156 g/m<sup>2</sup>. Further, the thickness of the protective layer was changed, thereby obtaining an intended silver halide color photographic light-sensitive material. It was recognized that the thus produced silver halide color photographic light-sensitive material of the present invention as well exerted the same excellent effects as in Example 2.

(Example 4)

Emulsion of the present invention having the same average equivalent sphere diameter as in the emulsion Em-F was produced. This emulsion satisfied all the requirements for the emulsion of the present invention. The emulsion Em-F of the 11th layer (high-speed green-sensitive emulsion layer) of the sample 101 was replaced with the above emulsion, and compound HET-3 of the present invention was added to the 11th layer (high-speed green-sensitive emulsion layer) in an

amount of 0.156 g/m<sup>2</sup>. Further, the thickness of the protective layer was changed, thereby obtaining an intended silver halide color photographic lightsensitive material. It was recognized that the thus produced silver halide color photographic lightsensitive material of the present invention as well exerted the same excellent effects as in Example 2.

5